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13. ABSTRACT (Maximum 200 words) Nucleation and growth of diamond were studied using microwave plasma, hot filament, and oxy-acetylene flame assisted CVD techniques. High quality, as indicated by IR absorption and Raman spectra, diamond was achieved for optical applications. Sequential deposition and etching was applied to achieve high growth rate while maintaining good diamond quality. By the use of a high power density microwave plasma, high rate, up to 50 um/h, growth of diamond was achieved in a broad range of substrate temperature up to 1500C and methane concentration near 100%. RF plasma induced negative bias was applied to achieve high density diamond nucleation on electrically insulating optical windows such as sapphire.				
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DIAMOND DEPOSITION BY CONTROLLED
NUCLEATION AND GROWTH

A Final Report
for
Contract No. N000014-90-J-1921
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Diamond Deposition by Controlled Nucleation and Growth

Final Report for Contract No. N00014-90-J-1921, R&T Project No. irmt029---01

Period Covered: April 1, 1990 - September 30, 1993

1. Introduction

The goals of this project include the better understanding of critical processing parameters and the exploration of innovative approaches to the nucleation of high density diamond crystallites and the growth of these diamond crystallites at a high rate to form optical quality diamond films and plates. Auburn University researchers participated in a team effort initiated by Dr. Bob Schwartz and later managed by Dr. Dan Harris aiming at the manufacturing of high performance diamond optical components for IR applications. Progress made every year was reported in the annual Tri-Service Diamond Dome and Window Research and Development Program Meeting. The last meeting before this project expired was held in Naval Warfare Center, Silver Springs, Maryland on September 21-23, 1993. Auburn University researchers attended these annual meeting and actively participated in the technical discussion.

During the period of this project, a number of diamond deposition techniques, including microwave plasma enhanced CVD, hot-filament assisted CVD, and combustion flame CVD, were explored to promote the deposition of high quality diamond. This report summarizes the latest technical progress made during the period of this project.

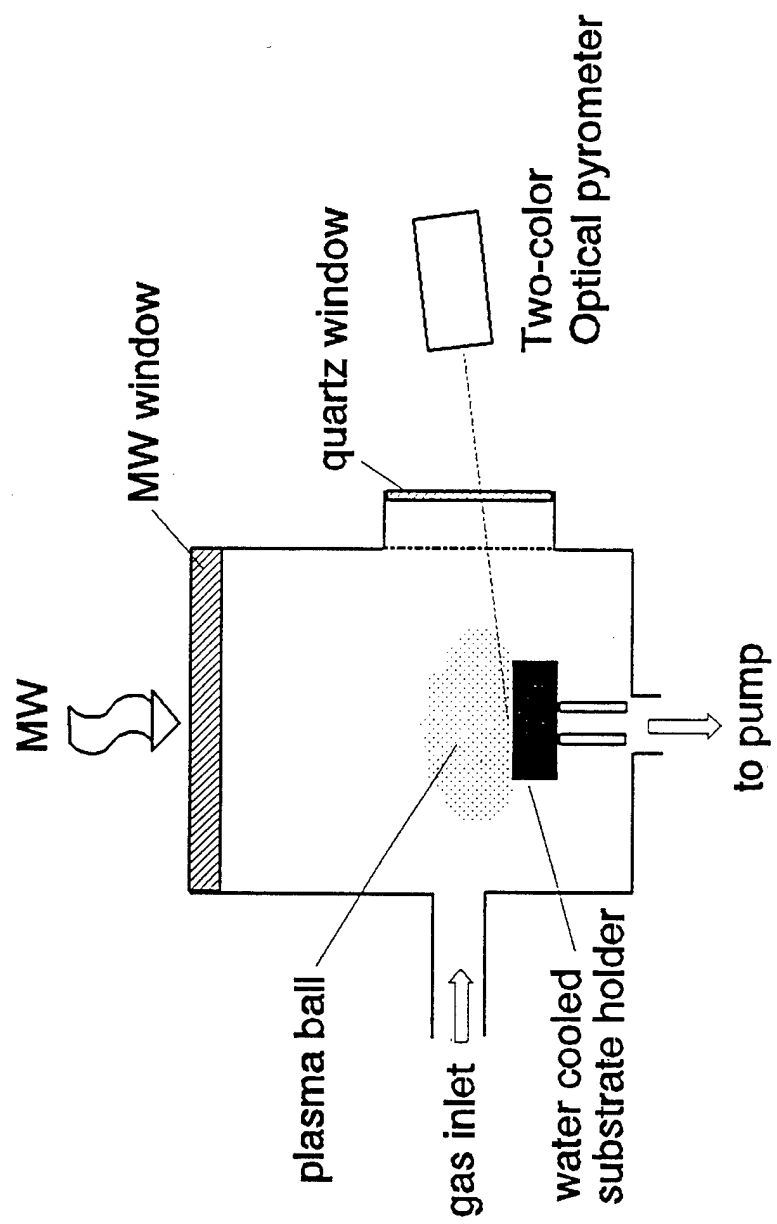


Figure 1. Microwave Plasma Enhanced Chemical Vapor Deposition Reactor.

2. Microwave Plasma Enhanced CVD of Diamond

A microwave plasma enhanced CVD reactor was designed and built by graduate students in Auburn University for this research. It consists of a 5kW microwave generator, a cylindrical microwave cavity, waveguides, pumping, gas handling, and temperature controlling equipment. Substrates including silicon, molybdenum, quartz, and sapphire were used for the study.

2.1 High Power Density Microwave Plasma Enhanced CVD of Diamond

The substrate holder inside the microwave plasma CVD reactor (see Figure 1) was modified so that an efficient cooling of the substrate was achieved allowing the application of a high power density of microwave to energize the plasma for diamond deposition. The substrates were made of threaded molybdenum rods. The molybdenum rods screwed into a water cooled copper block to obtain low thermal resistance between the diamond growing surface and the water cooled copper block. The molybdenum rod was only 1.2 cm in diameter. By increasing the gas pressure, the plasma ball formed by the microwave power became smaller in size. The applied power was thus absorbed by a smaller volume of the plasma leading to a higher power density (watts per cubic centimeter) plasma that could dissociate a high fraction of the gas molecules in the mixture. Because of the small plasma ball, the microwave power needed to study the high power density microwave plasma enhanced diamond CVD was less than 2kW.

2.1.1 Diamond Deposition in a Mixture of Hydrogen and a High Concentration of Methane

Most of reported microwave plasma enhanced chemical vapor deposition of diamond used

0.5 to 3% methane diluted in hydrogen as the feed gas and achieved a diamond growth rate of at most a few micrometers per hour. When the methane concentration exceeded a few percents diluted by hydrogen, diamond could not be deposited. The critical parameter in this process is the atomic hydrogen concentration. If most of the hydrogen in the gas feed remains in its molecular state, the flux of useful atomic hydrogen impinging the diamond growing surface is low and can not suppress the non-diamond deposition on the substrate. By using a high power density plasma, a much larger fraction of the hydrogen fed into the reactor is dissociated into atomic hydrogen making it possible for diamond to grow even if the methane concentration is much higher than a few percent.

At the normally reported substrate temperature of 900C, the diamond growth rate started at a few micrometers per hour for 1-3% of methane diluted by hydrogen. As the methane concentration increases, the diamond growth rate increases to about 10 micrometers per hour at 18% methane diluted by hydrogen. The diamond growth rate continues to increase as the methane concentration increases above 18% at a smaller rate of increase. This is shown in Figure 2.

Diamond Films deposited in methane concentration from 1% to 100% are shown in Figure 3. Well faceted diamond grains can be seen on the films deposited in methane concentration as high as 80%. The film deposited in 100% methane shows rounded grains. The Raman spectra for diamond films shown in Figure 3 are shown in Figure 4. The diamond Raman peak can be clearly seen on these spectra including the one for 100% methane. Although the background of the Raman spectra corresponding to diamond films deposited at a high methane shows a strong signal, the diamond peak is also strong and clear indicating the deposition of diamond under these conditions. The feasibility of growing diamond in a high methane concentration provides us with the possibility of depositing diamond films at high rates. Study is being conducted to improve the quality of

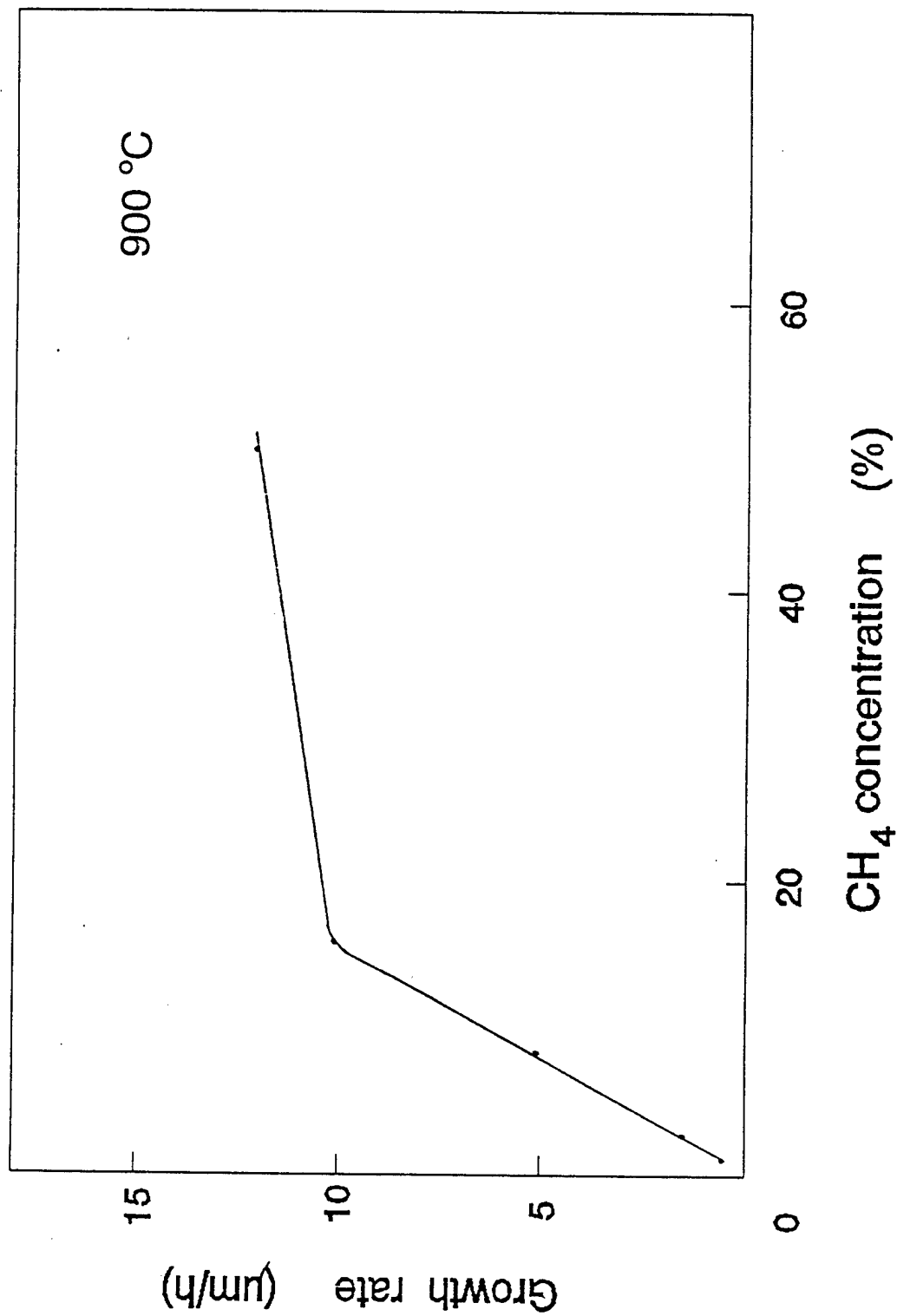
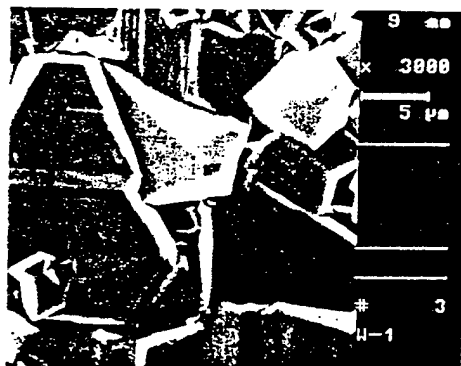
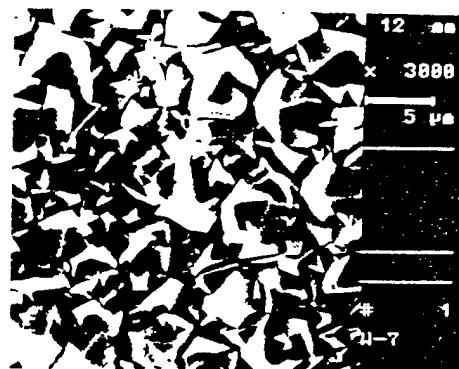


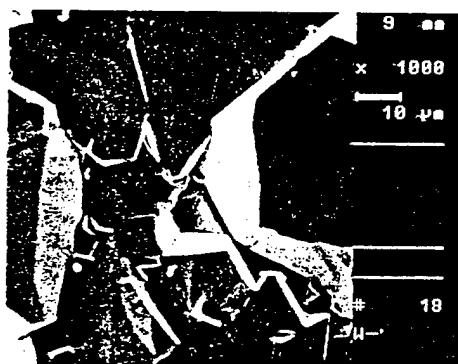
Figure 2. Diamond growth rate vs methane concentration at substrate temperature 900 °C.



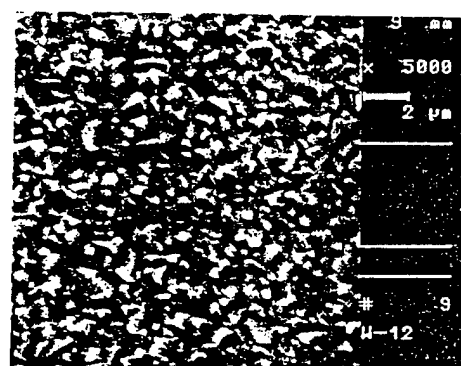
(a) 1% CH_4



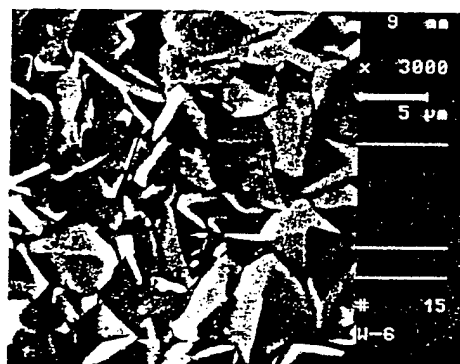
(d) 50% CH_4



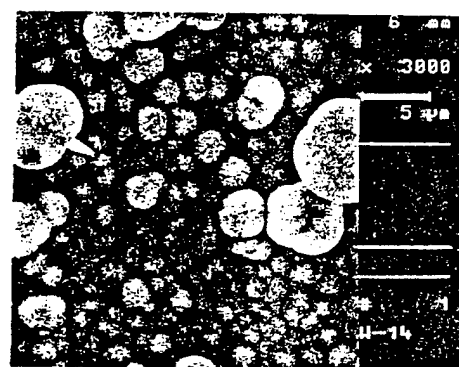
(b) 3% CH_4



(e) 80% CH_4



(c) 16% CH_4



(f) 100% CH_4

Figure 3. SEM photographs of diamond films deposited by microwave plasma CVD at 150 torr gas pressure and 900 C substrate temperature in gas mixtures of CH_4 and H_2 .

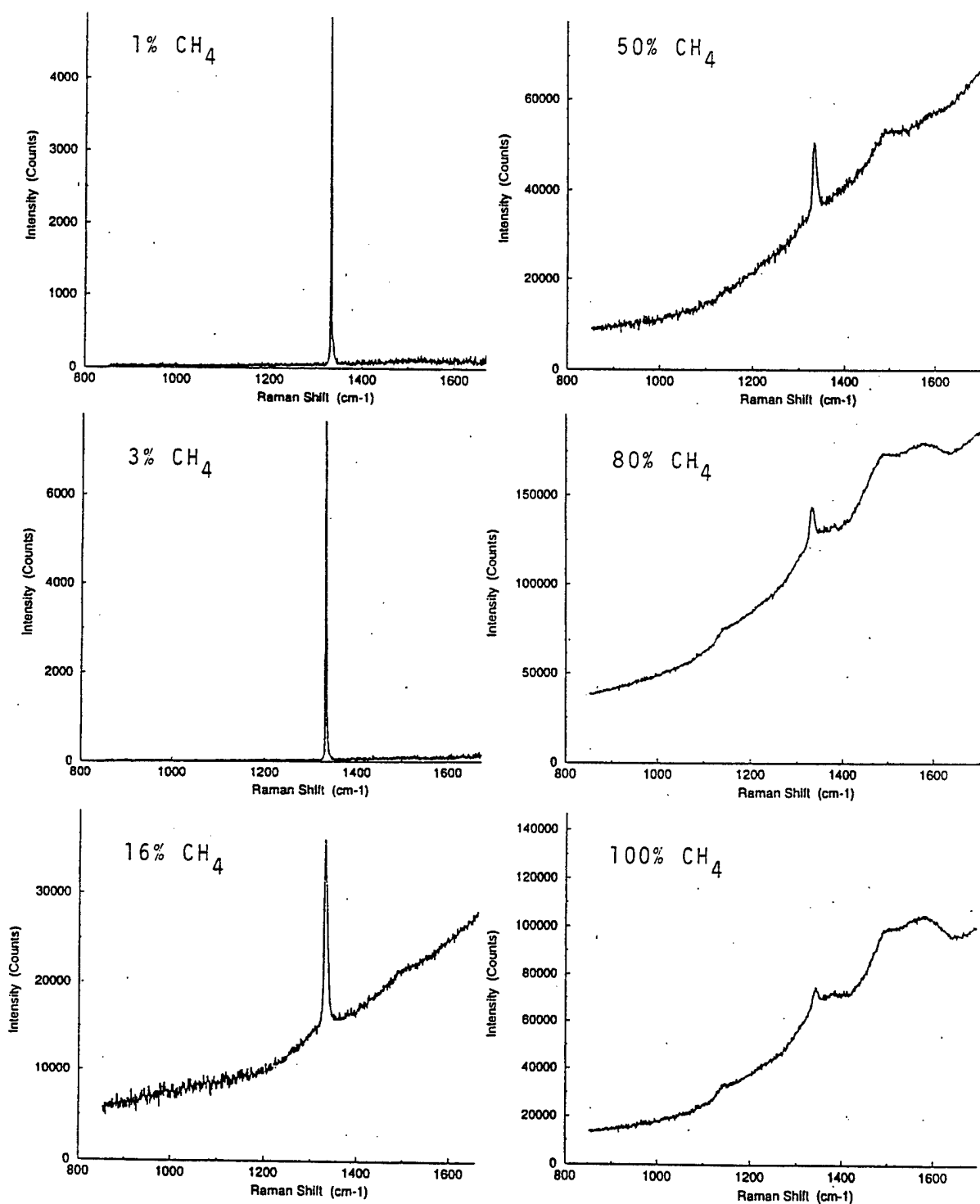


Figure 4. Raman spectra of diamond films deposited by microwave plasma CVD at 150 torr and 900 C substrate temperature in gas mixtures of CH₄ and H₂.

diamond deposited in a high concentration of methane so that growth rate can be increased without sacrificing the quality of diamond.

2.1.2 Diamond Deposition at Substrate Temperature above 1000 C

When a medium to low power density microwave plasma is applied to deposit diamond, it is well known that diamond growth rate increases with substrate temperature until it reaches the maximum growth rate. When the substrate temperature exceeds that temperature, the diamond growth rate decreases and eventually drops down to zero. The substrate temperature at which the maximum growth rate of diamond is achieved depends on other process parameters such as power density, gas pressure, gas feed composition, and substrate materials.

The decrease in the diamond growth rate has to do with the short lifetime of diamond precursors that stay on the diamond growing surface at high temperatures and the insufficient impingement flux of atomic hydrogen for sustaining the diamond structure on the diamond growing surface. This barrier can be overcome by the application of a high power density microwave plasma to supply a high flux of atomic hydrogen as well as diamond precursors to the diamond growing surface leading to a high growth rate at substrate temperatures well above 1000 C. Shown in Figure 5 are the diamond growth rates for substrate temperatures ranging from 500 C to 1500 C. The methane concentration used was 16% diluted by hydrogen. The diamond growth rate increases with substrate temperature and reaches a rate as high as 50 μm per hour. Diamond films deposited at substrate temperatures ranging from 550C to 1600C are shown in Figure 6. From Figure 6, well faceted diamond grains can be seen for diamond films deposited at substrate temperatures as high as 1450C. Raman spectra corresponding to diamond films shown in Figure 6 are shown in Figure 7.

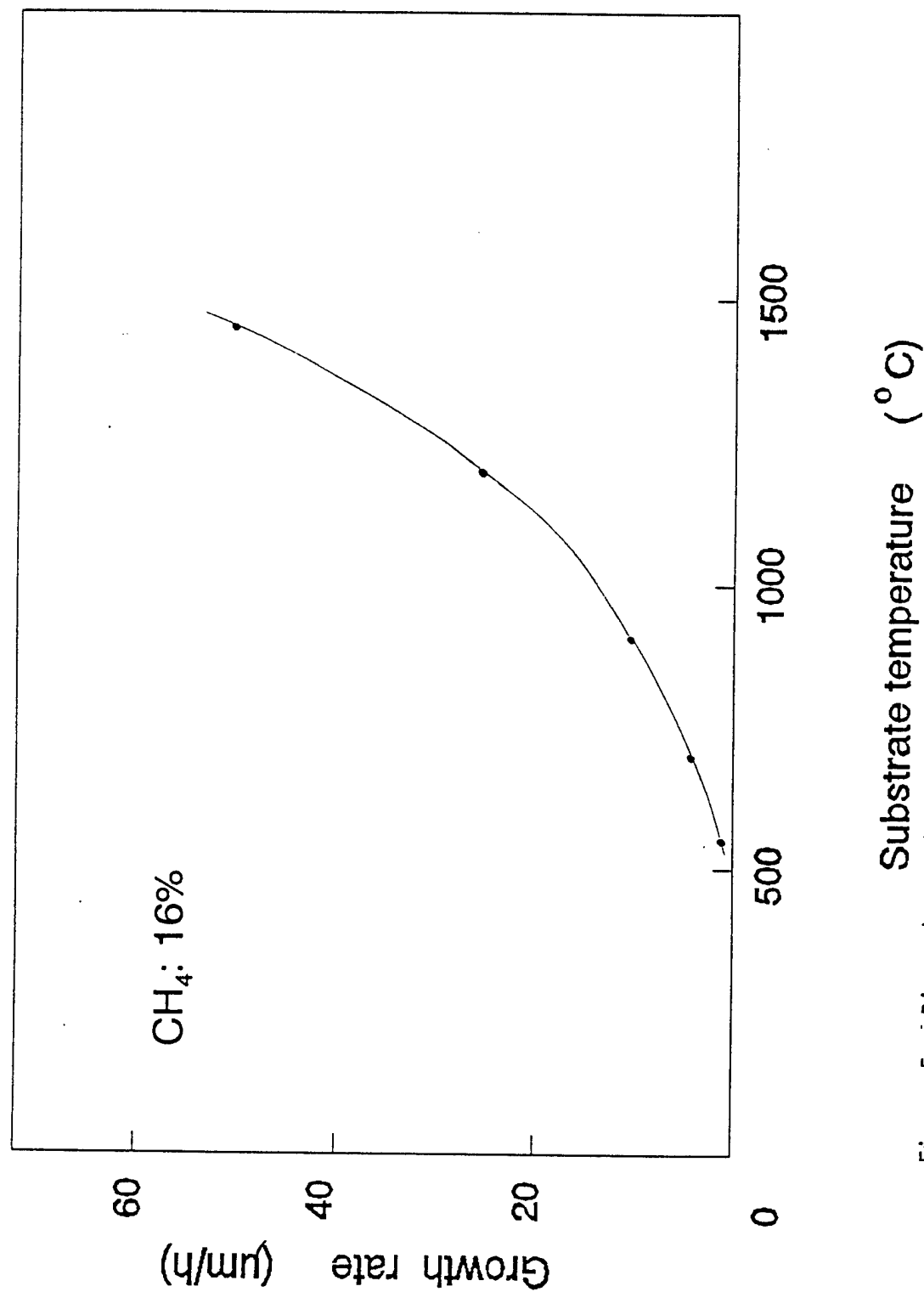
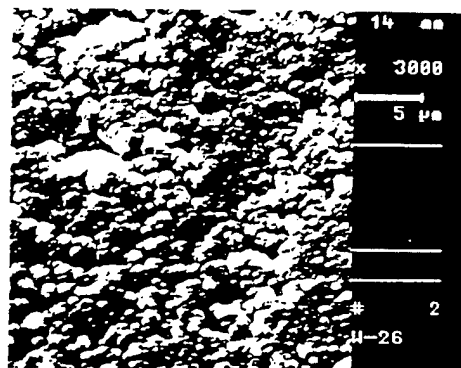
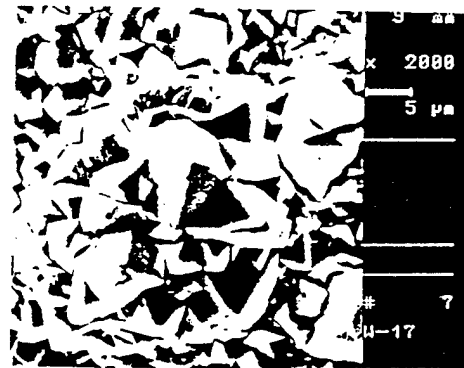


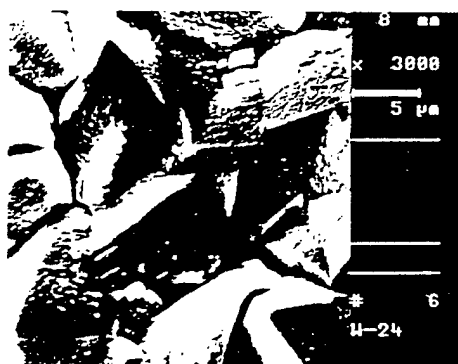
Figure 5. Diamond growth rate vs substrate temperature for 16% methane diluted by hydrogen.



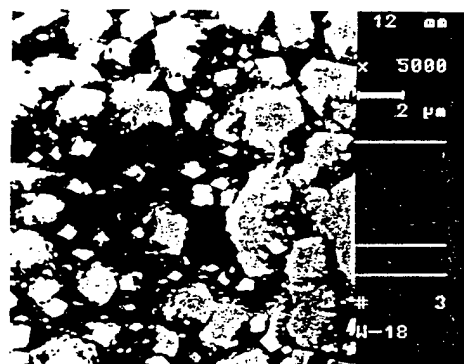
(a) 550 C



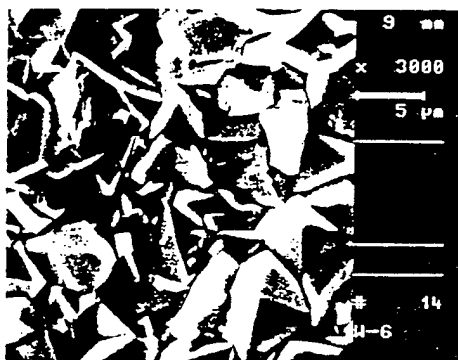
(d) 1200 C



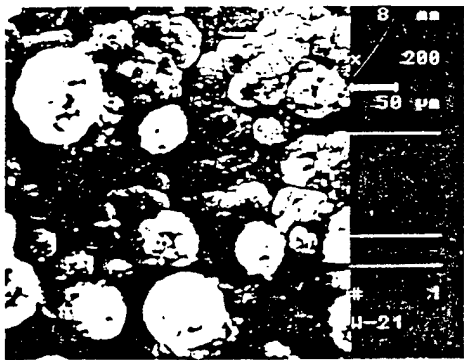
(b) 700 C



(e) 1450 C



(c) 900 C



(f) 1600 C

Figure 6. SEM photographs of carbon films deposited by microwave plasma CVD at gas pressures between 100 and 150 torr in a gas mixture of 16% CH_4 diluted by H_2 .

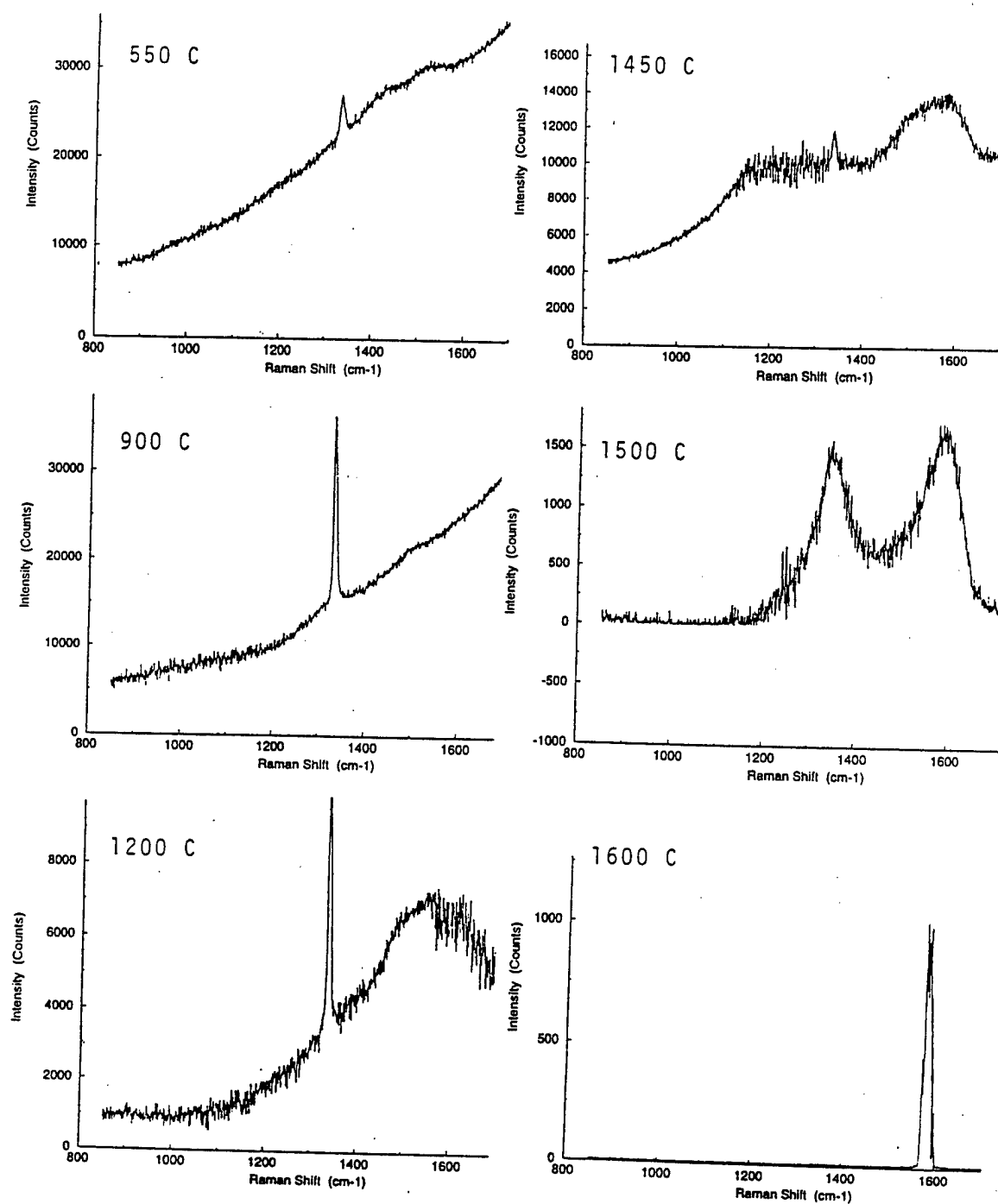


Figure 7. Raman spectra of carbon films deposited by microwave plasma CVD at gas pressure between 100 and 150 torr in 16% CH₄ diluted by hydrogen.

For films deposited at substrate temperatures up to 1450 C, the diamond Raman peak can be clearly seen on the spectra. Even at 1200 C, the Diamond peak is still very intense indicating that high temperature diamond growth by CVD is possible. At the substrate temperature of 1600C, the carbon film deposited shows only the graphite peak indicating that graphite instead of diamond is grown at this temperature.

2.1.3 Diamond Deposition at Substrate Temperature below 600 C

Deposition of diamond at low substrate temperatures has been demonstrated by many research groups. The main bottleneck with the deposition of diamond at low substrate temperatures is the low growth rate. The diamond growth rate decreases exponentially with substrate temperature and reaches a rate that is too low for practical applications.

By the use of the high power density microwave plasma, diamond deposition was achieved at a rate exceeding 1 micrometer per hour at the substrate temperature of 500C. The high growth rate was made possible by the use of a methane concentration as high as 16%. Shown in Figure 8 is the diamond growth rate as a function of the methane concentration at a substrate temperature of 500C. The diamond growth rate is almost a linear function of the methane concentration. The diamond films deposited at a low substrate temperature at 550C also show clear diamond Raman peaks on their corresponding Raman spectra shown in Figure 9. Because of the small grain size for diamond grown at such a low substrate temperature, the diamond Raman spectra have much weaker Raman peaks with a strong background signal. Nevertheless, the carbon films deposited are diamond and the growth rate of one micrometer per hour is more than acceptable for most coating applications.

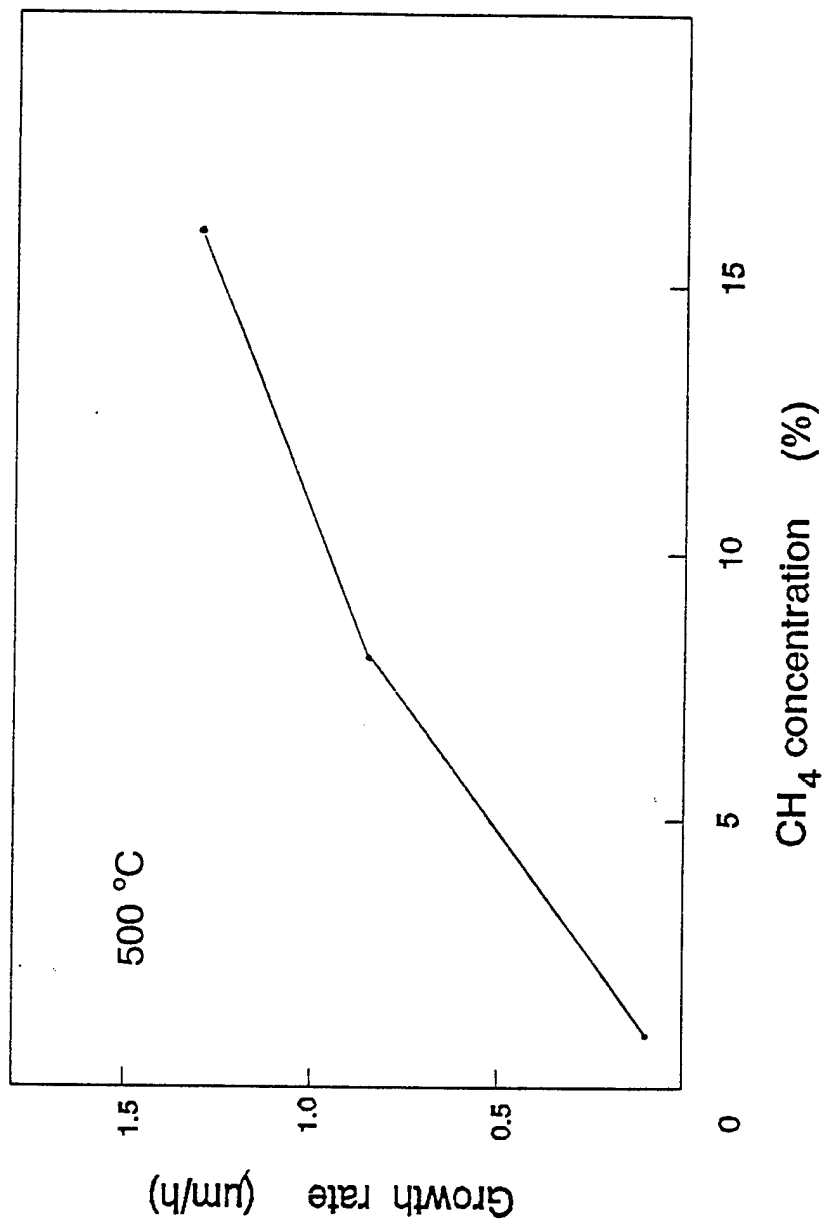


Figure 8. Diamond growth rate vs methane concentration at the substrate temperature of 500 C.

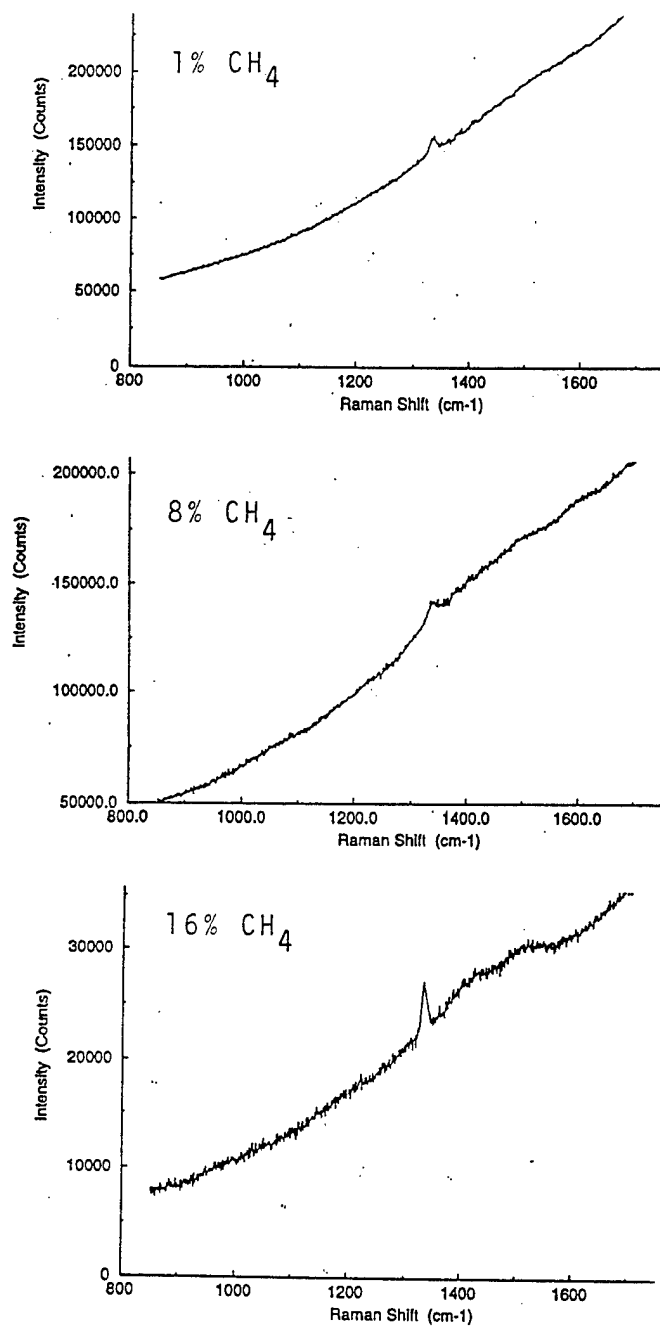


Figure 9. Raman spectra of diamond films deposited by microwave plasma CVD at 100 torr and 550 C substrate temperature in gas mixtures of CH₄ and H₂.

2.2 Diamond Coatings on Quartz and Sapphire Optical Windows

Because of the large difference in the coefficient of thermal expansion between diamond and substrates such as quartz and sapphire, diamond deposited on these substrates tends to crack and lose adhesion to the substrates. In order to achieve a continuous coating of diamond, a high density of diamond nucleation is needed. Biased nucleation is a good technique for achieving a high density of diamond nucleation. Since Quartz and Sapphire are electrical insulators, a DC bias does not work. We have applied an RF bias to the substrate and achieved a continuous diamond coating on quartz and sapphire by first nucleating a high density of diamond crystallites and then grow a thin film of diamond coating. More details of this process can be found in Appendix 1.

3. Hot Filament Assisted CVD of Diamond

Hot filaments made of tungsten and tantalum were used to dissociate molecular hydrogen for diamond deposition. Hot filament CVD has its advantages of being inexpensive in capital investment and easy to be scaled up for large area diamond deposition. In order to promote the diamond growth rate we studied the critical process parameters for high rate diamond growth and explored means of maintaining high diamond quality.

3.1 Critical Process Parameters for High-Rate Deposition of Diamond by

Hot-Filament CVD Technique

High quality diamond was deposited at a rate higher than 16 $\mu\text{m/hr}$ using the hot filament CVD technique. By increasing the filament temperature, the methane concentration can be increased. This is similar to the application of a high power density to the microwave plasma enhanced diamond CVD process. In the case of hot filament CVD, the higher the filament temperature is, the higher

fraction of the hydrogen molecules are dissociated to produce atomic hydrogen. More details of the process can be found in Appendix 2.

3.2 Growth of Diamond by Sequential Deposition and Etching Process Using Hot

Filament CVD

In order to achieve a high rate diamond growth without sacrificing the quality, a sequential deposition and etching process was studied. During the deposition cycle, a high methane concentration diluted in hydrogen was used for high growth rate diamond deposition. During the etching cycle,, pure hydrogen was used to etch the non-diamond components that have been co-deposited during the deposition cycle. For a short cycling period, i.e., 10 seconds deposition and 10 seconds etching, high quality diamond films were deposited with growth rates several times higher than what was achieved using the continuous deposition process that produced similar diamond quality. More details of this process can be found in Appendix 3.

4. High Quality Flame-Deposited Diamond Films for IR Optical Windows

Combustion flame provides another simple way of deposition diamond films. This study is aimed at achieving optical quality diamond films using an atmospheric oxygen-acetylene flame.

The IR Absorption in polycrystalline diamond films deposited in oxygen-acetylene flames was characterized using the Fourier transform IR spectroscopy (FTIR). The one-phonon absorption coefficient in the region from 7 to 12 μm that is related to extrinsic defects in the diamond films shows a strong dependence on the flame conditions as well as the substrate temperature. A high degree of diamond crystalline perfection, as judged from the undetectable one-phonon absorption, is achieved under the optimized deposition conditions for our flame set-up. This is further supported by the sharp Raman peak at 1332 cm^{-1} as well as the high purity in crystalline orientation according

to the X-ray diffraction pattern measured for the high quality diamond films. Optimal deposition conditions produce diamond films with a lower degree of secondary nucleation than is found in the lower quality diamond deposits. More details of this process and discussion can be found in Appendix 4.

Diamond-Coated Quartz and Sapphire Optical Windows

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Key words: CVD diamond, nucleation density, thin coating

Thin and smooth diamond films have been deposited on unseeded and electrically insulating substrates such as quartz and sapphire that serve as optical windows. High nucleation density, greater than 10^{10} particles/cm² required for obtaining smooth coating of diamond was achieved on these substrates by using a combined radio-frequency (RF) and microwave plasma nucleation technique followed by a short duration of diamond deposition in a microwave plasma. The RF power applied to the substrate induces a negative electrical bias that helps to retain carbon and hydrocarbon species on the substrate surface as well as promote the etching of nondiamond deposition, thus leading to enhanced nucleation. The thin pin-hole-free diamond film adhered well to these substrates. The diamond coatings obtained on substrates such as quartz and sapphire were characterized using optical microscopy, SEM, XPS, and Raman scattering spectroscopy.

1. Introduction

Diamond's optical transparency combined with its excellent mechanical and thermal properties makes it a sound choice for optical applications. Although single-crystal diamond is a strong contender for use as an optical component, the cost and size of available single-crystal diamond curtail its use in many situations. The recent development of chemical vapor deposition of diamond has paved the way for the fabrication of free-standing polycrystalline diamond films⁽¹⁾ that have good optical transparency as well as the coating of thin and high-quality diamond films on optical windows.

One of several problems associated with the polycrystalline CVD diamond films is the large scattering of an incident beam by the relatively rough diamond surface. Normally the rough surface of CVD diamond must be polished to certain tolerable limits for its use as an optical window. Currently the exorbitant cost of polishing CVD diamond governs the price of diamond optical windows. Therefore, it is desirable to grow diamond films that have low surface roughness by increasing the diamond nucleation density prior to growth. The order of surface roughness is determined by the distance between the diamond nuclei formed on the substrate. Thus, the higher the nucleation density is, the smoother the film and the lower the light scattering by the film. Wild et al. have demonstrated the low reflectance of a thin and smooth diamond film obtained by increasing the diamond nucleation density by ultrasonic agitation.⁽²⁾

Many techniques that exist at present for increasing nucleation density of diamond on substrates rely mainly on diamond seeding or the damaging of the surface. Such surface-destructive techniques are not only inconvenient but also have limited applications. Recently Yugo et al. demonstrated the effect of applying a negative DC bias to the substrate for enhancing diamond nucleation on mirrorlike silicon substrates in a microwave plasma CVD system.⁽³⁾ The DC substrate biasing scheme for increasing diamond nucleation density is limited to electrically conducting or semiconducting substrates; however, an RF self-bias technique can also be utilized to heavily nucleate diamond on unseeded insulating substrates.

In this paper we have investigated the means of achieving optically smooth and thin diamond coatings that are adherent on unseeded quartz and sapphire substrates that serve as optical windows.

2. Experimental

Figure 1 shows a microwave plasma CVD (MPCVD) system with an RF biasing network. A 600 W magnetron was mounted to the copper waveguide system to deliver the microwave power to form a plasma in a 50-mm-diameter quartz tube that passed through the center of a rectangular waveguide. The amount of reflected power was controlled by adjusting a sliding short and tuning screws. An automatic interlock system was designed to shut off the high-voltage power supply to the magnetron, and stop the gas flow to the chamber in case of a large reflected power or in case of an increase in the chamber pressure above a certain set point. Gases such as methane, hydrogen, and oxygen were fed into the chamber through electronic mass flow controllers (MFCs).

A molybdenum substrate holder was electrically connected to an RF generator. A grounded spiral tantalum electrode was placed approximately 4~6 cm from the substrate holder. RF power of less than 100W was applied to the substrate through a coupling capacitor that blocked the DC biasing voltage while it allowed RF to pass through without significant attenuation. The negative bias at the substrate was measured by a voltmeter placed across an inductor capacitor network as shown in Fig. 1. This RF-induced negative self-bias scheme has previously been used for plasma etching.⁽⁴⁾

Substrates were initially nucleated with diamond by using a combined RF and micro-

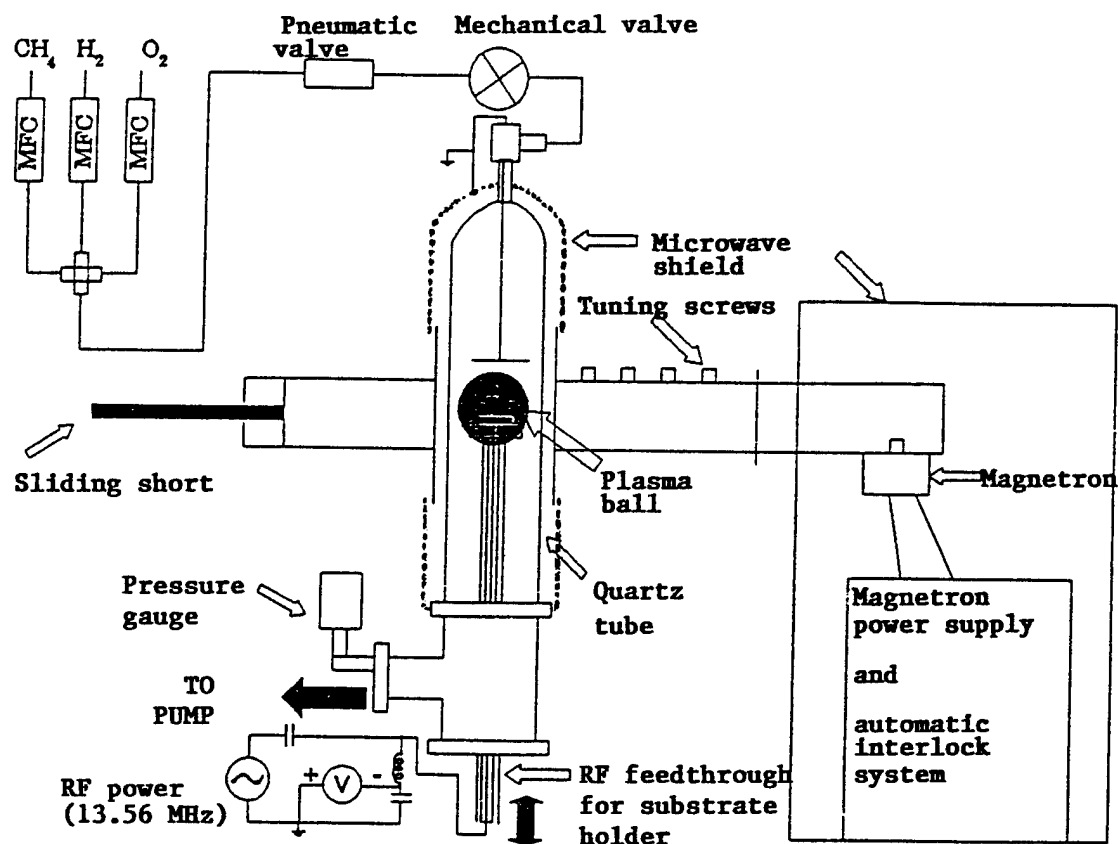


Fig. 1. Microwave plasma CVD reactor with RF biasing network.

wave nucleation technique in a high (20% ~ 40%) methane concentration environment. This was followed by a diamond deposition step using 0.2% methane in hydrogen for approximately 30 minutes. The typical nucleation and deposition parameters used are shown in Table 1.

Table 1
Typical nucleation and deposition parameters.

Parameter	Nucleation	Growth
RF-induced DC self-bias (V)	-100	-
RF power (W)	< 100	-
Microwave power (W)	~ 450	600 ~ 750
Reactor pressure (torr)	50 ~ 60	20 ~ 30
Substrate temperature (°C)*	900 ~ 950	900 ~ 950
CH ₄ in H ₂ (%)	20~40	0.2 ~ 1.0
Exposure time (min)	< 5	15 ~ 30

*measured by an optical pyrometer.

3. Results and Discussion

Figure 2 shows an SEM micrograph of the diamond film obtained on quartz after 3 minutes of nucleation using 20% methane in hydrogen and 30 minutes of deposition using 0.2% methane in hydrogen. The figure reveals that the thin pin-hole-free diamond film obtained has a nucleation density greater than 10^{10} particles/cm². A similar coating was also obtained on sapphire. It is estimated that the thickness of the film is about 0.5 μ m. Figure 3 shows the Raman spectrum obtained for the coating shown in Fig. 2. The Raman spectrum reveals the characteristic diamond peak and a small broad band indicating the inclusion of nondiamond components in the diamond film. These inclusions may be due to the short exposure of substrates to the relatively high methane concentration environment during the nucleation step.

Figure 4(a) shows the thin diamond film on a quartz substrate obtained by increasing the methane concentration during the nucleation step to 40%. Diamond deposition was then carried out for 15 minutes in 1% methane in hydrogen. Figure 4(b) shows the XPS spectrum obtained for the diamond thin film in Fig. 4(a). Clearly, large amounts of nondiamond components are present in the diamond film of Fig. 4(a). Poor optical transparency was observed for diamond films deposited using various methane concentrations ($> 0.2\%$) after a nucleation step using 40% methane in hydrogen. We believe that this may be due to large amounts of nondiamond components deposited during the nucleation step that are not completely removed by the subsequent deposition step.

Our studies have indicated that by increasing the methane concentration in hydrogen

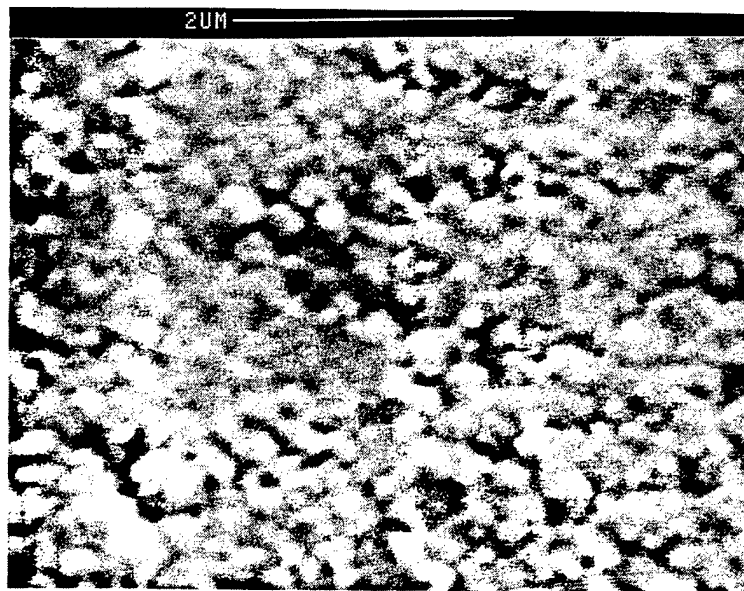


Fig. 2. Thin and smooth diamond coating obtained on unseeded quartz substrate after 3 minutes of nucleation followed by 30 minutes of diamond deposition. The thickness of the film is about 0.5 μ m.

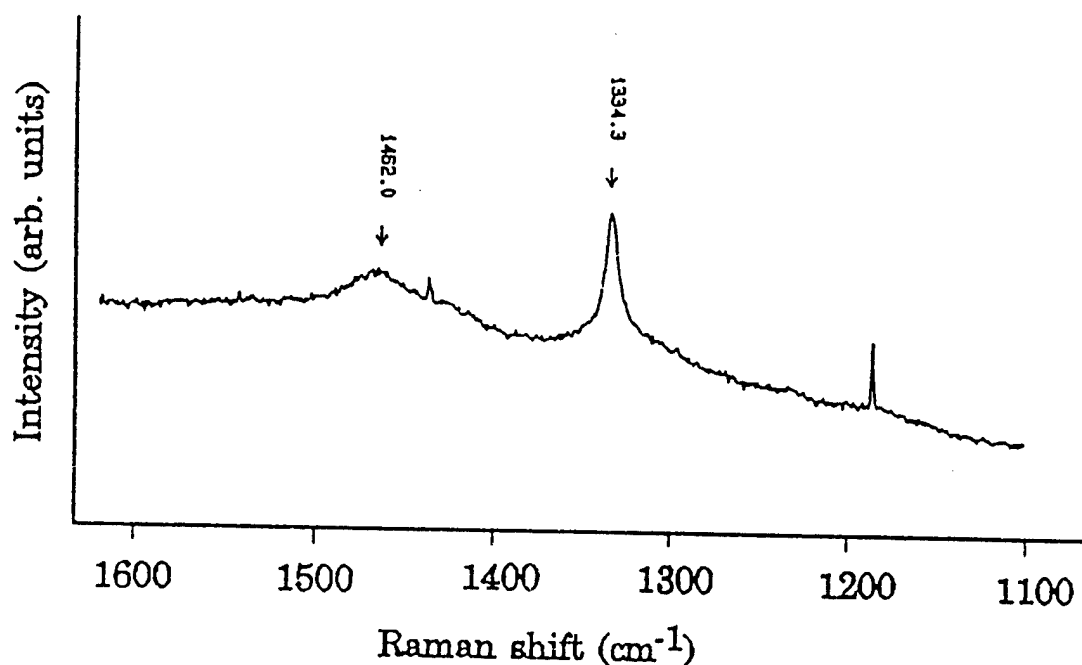


Fig. 3. Raman spectrum for the diamond coating on quartz shown in Fig. 2.

during the initial nucleation step, faster nucleation can be obtained, but, with slightly more inclusions of nondiamond components. Conversely, using relatively low methane concentration in hydrogen during the nucleation step not only reduces the nucleation density but also increases the time required for nucleation. This disadvantage is offset by the decrease in the amount of nondiamond components in the final diamond film.

Figure 5 shows an optical photograph of (a) an untreated optically transparent quartz substrate, (b) a thin diamond film coated uniformly on a quartz substrate after nucleation and deposition, and (c) quartz substrate surface after 3 minutes of diamond nucleation in 20% methane in hydrogen. The coating obtained on sapphire was similar to that obtained on quartz under the same nucleation and deposition conditions. By using 20% methane in hydrogen during nucleation and 0.2% methane in hydrogen during growth, we achieved a high nucleation density required for smooth diamond film with less light scattering and fewer inclusions of nondiamond components in the film required for better optical transmission.

4. Conclusions

Thin and smooth diamond films were deposited on optical windows such as quartz and sapphire by first achieving a high diamond nucleation density on these unseeded substrates by a combined RF and microwave plasma technique and then by diamond deposition at a relatively low methane concentration. Higher methane concentration during the nucleation step leads to faster nucleation but with more inclusions of nondiamond components.

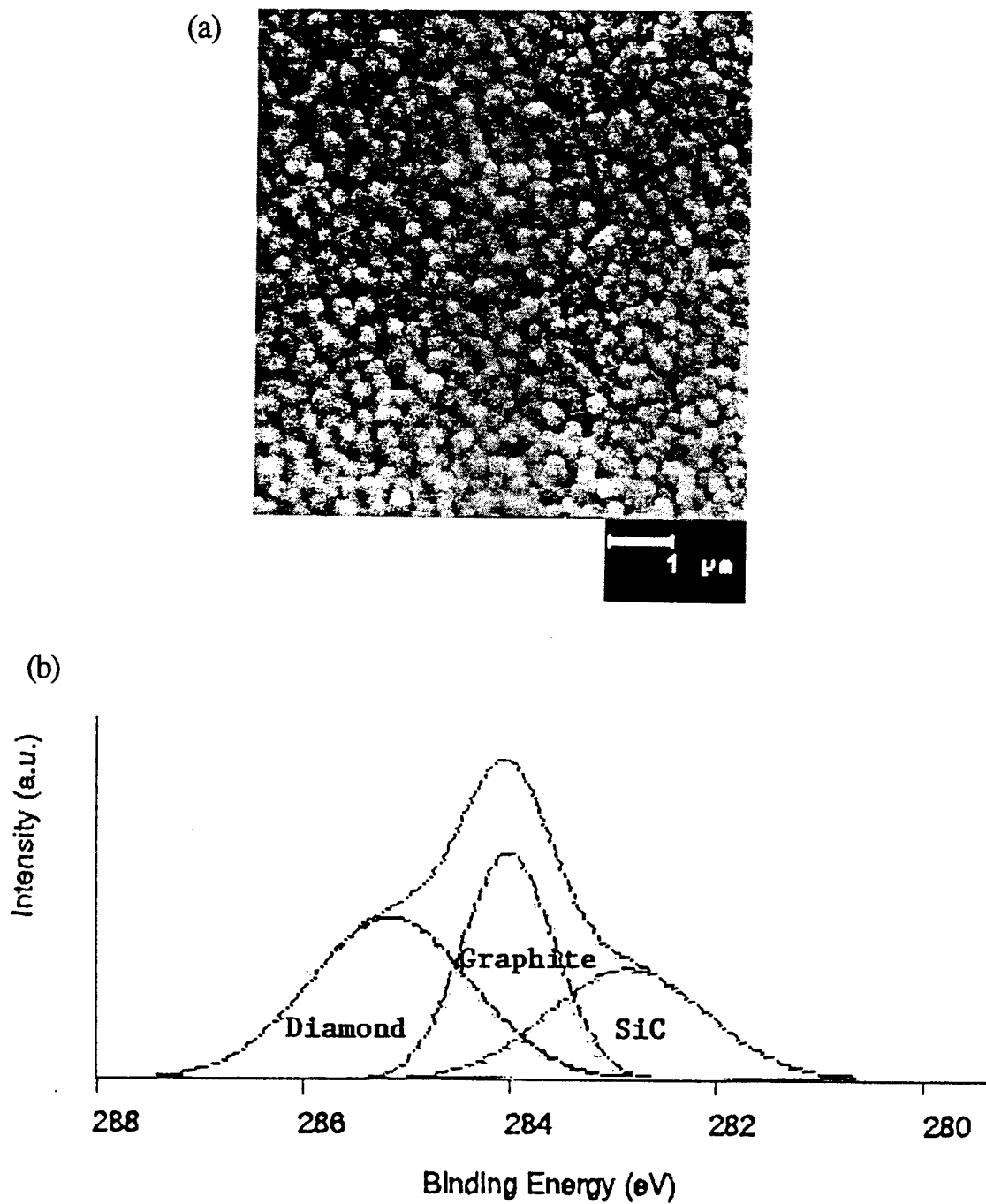


Fig. 4. (a) SEM micrograph of quartz substrate surface after 5 minutes of nucleation in 40% methane in hydrogen and 15 minutes of deposition in 1% methane in hydrogen. Diamond nucleation density is on the order of 10^{10} particles/cm². (b) XPS C(1s) core level spectrum showing diamond and graphite present in the film obtained in (a).

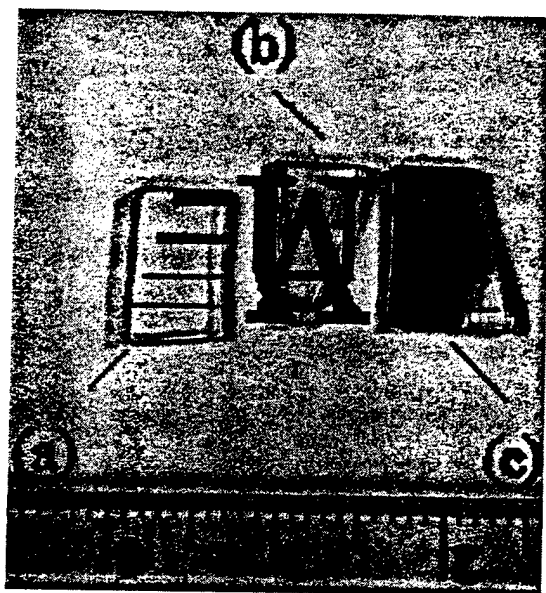


Fig. 5. (a) An unseeded quartz substrate, (b) quartz substrate uniformly coated with a thin diamond film, and (c) quartz substrate surface after 3 minutes of nucleation using 20% methane in hydrogen.

Conversely, a smaller amount of nondiamond components in the diamond film can be obtained by decreasing the methane concentration during the nucleation step. For better optical transparency of the diamond film, the concentration of methane in the nucleation step was lowered to 20% and that during growth was lowered to 0.2%. We have successfully obtained thin diamond coatings on quartz and sapphire substrates.

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Critical Process Parameters for High-Rate Deposition of Diamond by Hot-Filament CVD Technique

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The effects of process parameters such as the filament temperature, the filament-substrate distance and the gas composition and pressure on the CVD diamond crystallinity and growth rate have been investigated. High filament temperature and short filament-substrate distance at an appropriate high reactor pressure are advantageous for high-rate deposition of high-quality diamond. The growth rate increases with increasing filament temperature and decreasing filament-substrate distance. At a filament temperature of around 2600°C and a filament-substrate distance of 1 mm, a high concentration (7%) of methane (CH₄) was used for high-quality diamond deposition. The growth rate exceeded 16 µm/h at a reactor pressure of 200 Torr.

1. Introduction

Since hot-filament chemical vapor deposition (CVD) is relatively simple and can be used for large-area diamond deposition,⁽¹⁾ it has become one of the most common techniques for the manufacture of diamond films.⁽²⁾ However, the low growth rate, on the order of 1 µm/h or less, for high-quality diamond growth is still a barrier to a wider range of applications. There are several reports concerning the enhancement of the growth rate of diamond films

in the hot-filament CVD technique. For example, the application of a positive bias on the substrate,⁽³⁾ the use of alcohol, acetone or other organic compounds,⁽⁴⁾ the generation of a DC plasma between the filament and the substrate,⁽⁵⁾ and the optimization of the filament materials and temperatures⁽⁶⁾ have been reported. In this paper, we report some critical process parameters for high-rate growth of diamond without sacrificing the diamond quality.

2. Experimental

The hot-filament CVD system used in this study is shown schematically in Fig.1. Tungsten wires 0.25 mm in diameter were used as the filaments. They were carburized in a mixture of methane (CH_4) and hydrogen before diamond deposition experiments were carried out. First the appropriate electrical current was determined by increasing the current applied to carburized filament until the filament failed due to overheating. The experiments were then carried out by applying a slightly lower electrical current to a new set of carburized

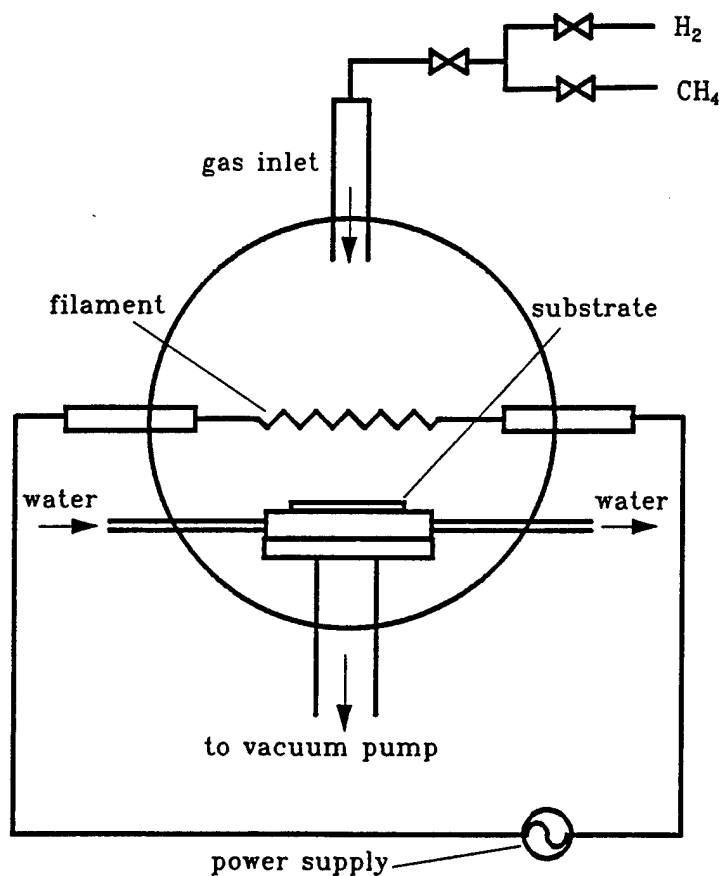


Fig.1. Schematic diagram of a hot-filament CVD system.

tungsten wires of the same diameter. The filament temperature during diamond growth was measured by an optical pyrometer and was around 2600°C. A molybdenum substrate holder was used for the deposition. The substrate holder temperature was controlled by hot filament, cooling water, distance between the filament and the substrate, and the spacer inserted between the substrate holder and the water-cooled stage, and measured by a thermocouple inserted into the molybdenum substrate holder. Silicon substrates were ultrasonically agitated using 20~40 μm diamond powder before the deposition. The reaction conditions are shown in Table 1. The growth rate measurement and the characterization of the deposited diamond films were done by means of optical microscopy, scanning electron microscopy (SEM), and Raman scattering spectroscopy.

Table 1
Diamond film deposition conditions.

CH ₄ concentration in H ₂ -CH ₄	0.5 ~ 10%
Reactor pressure	10 ~ 500 Torr
Total flow rate	200 sccm
Filament temperature	2000 ~ 2600°C
Filament-substrate distance	1 ~ 5 mm
Substrate temperature	600 ~ 1000°C

3. Results and Discussion

Filament temperature is one of the most important parameters for hot-filament CVD of diamond. High filament temperature leads to the deposition of high-quality diamond at a high rate. We investigated the dependence of the diamond growth rate on CH₄ concentration at the filament temperature of around 2600°C, as shown in Fig.2. The reactor pressure was 50 Torr. The substrate holder temperature was 700°C. The filament-substrate distance was 2 mm. The diamond growth rate increased with increasing CH₄ concentration up to 5%. In contrast, the usual CH₄ concentration for achieving high-quality diamond deposition is lower than 1% when the filament temperature is around 2000~2200°C. With the use of a higher filament temperature, a higher CH₄ concentration was thus allowed for high-rate diamond deposition.^(6,7) This is a result of a higher concentration of atomic hydrogen being produced by filaments at a higher temperature.⁽⁸⁾ Therefore, high filament temperature is advantageous for high-rate diamond deposition without sacrificing the diamond quality.

The growth rate and crystallinity of diamond also depend strongly on the filament-substrate distance. Figure 3 shows the dependence of normalized diamond growth rate on the filament-substrate distance. The filament-substrate distance was varied from 5 mm to 1 mm while other conditions were unchanged. The growth rate increased with decreasing filament-substrate distance as a result of the higher densities of reactive species responsible for diamond growth on the substrate surface. Figure 4 shows the dependence of the normalized diamond growth rate on reactor pressure. The filament temperature was 2600°C, and the substrate holder temperature was 700°C. The growth rate at the reactor pressure of

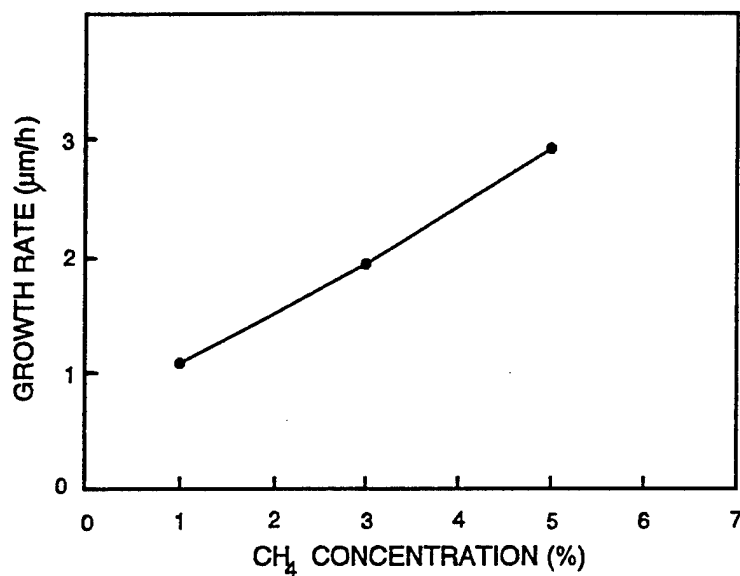


Fig. 2. Dependence of the diamond growth rate on CH_4 concentration at the filament temperature of 2600°C . The reactor pressure was 50 Torr. The substrate holder temperature was 700°C . The filament-substrate distance was 2 mm.

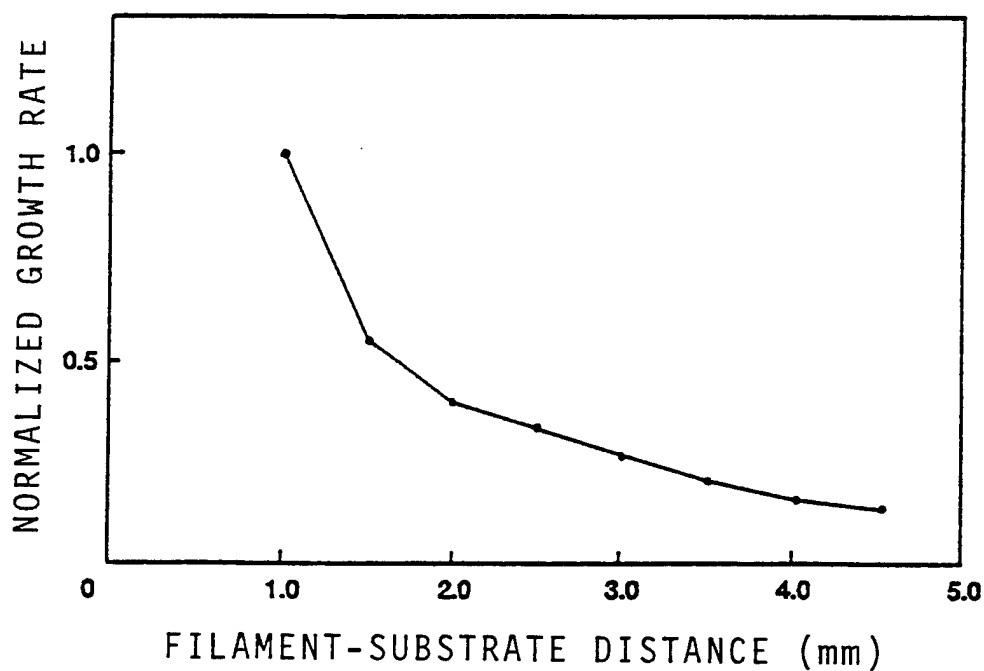


Fig. 3. Dependence of the normalized diamond growth rate on the filament-substrate distance. The filament temperature was 2600°C . The substrate holder temperature was 700°C .

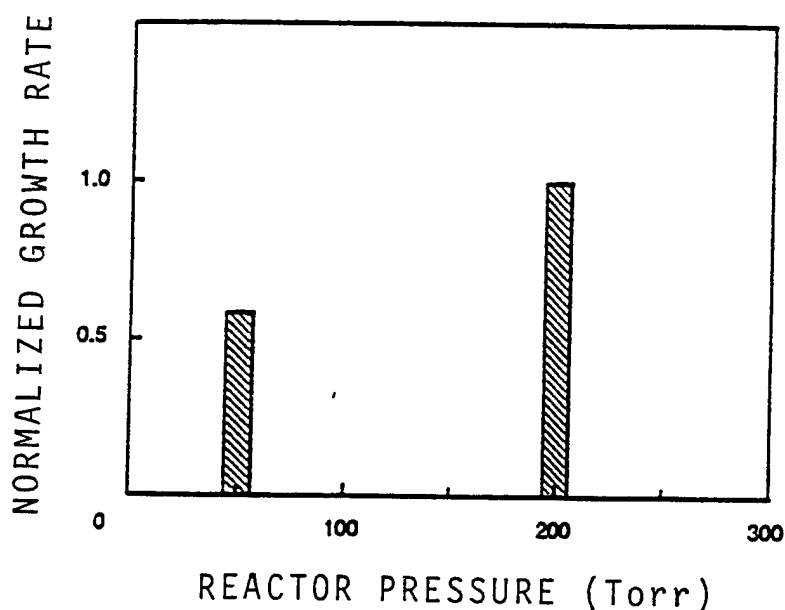


Fig.4. Dependence of the normalized growth rate of the diamond film on reactor pressure.

200 Torr is higher than that at 50 Torr. At the higher pressure, the densities of activated species for diamond deposition near the substrate are higher than those at the lower pressure. The growth rate of diamond film at a higher reactor pressure is thus higher than that at a lower pressure within the pressure range studied here.

Figures 5(a) and 5(b) show the SEM images of the diamond films deposited at CH_4 concentrations of 5% and 7%, respectively, at a filament temperature of 2600°C , a filament-substrate distance of 1 mm and a reactor pressure of 200 Torr. Both Fig.5(a) and Fig.5(b) show well-faceted diamond crystals. The growth rates are shown in Fig.5(c). The growth rate was increased by increasing the CH_4 concentration from 5% to 7% without sacrificing the quality of the diamond film. High-quality diamond films with growth rate greater than $16\text{ }\mu\text{m/h}$ were achieved. The diamond film deposited in 9% CH_4 diluted by H_2 with other conditions unchanged, showed some nondiamond inclusions. A CH_4 concentration of around 7% was found to be the maximum concentration for obtaining high-quality diamond deposition under the above-mentioned conditions using our hot-filament CVD reactor. The Raman spectrum for the diamond film shown in Fig.5(b) shows a sharp diamond peak at 1332 cm^{-1} (see Fig.6).

4. Conclusions

For hot-filament CVD, the growth rate and crystallinity of the diamond film depend strongly on the filament temperature, the filament-substrate distance, the methane concentration, and the reactor pressure. By increasing the filament temperature, the maximum allowed CH_4 concentration for high-quality diamond deposition is also increased. Higher

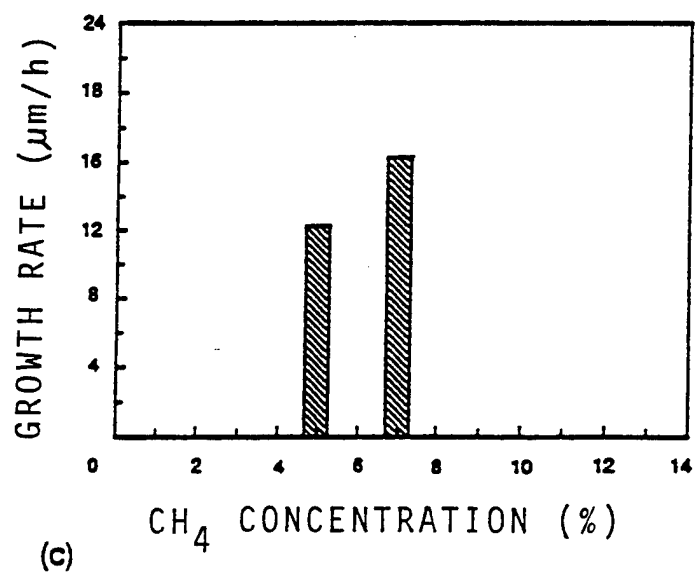
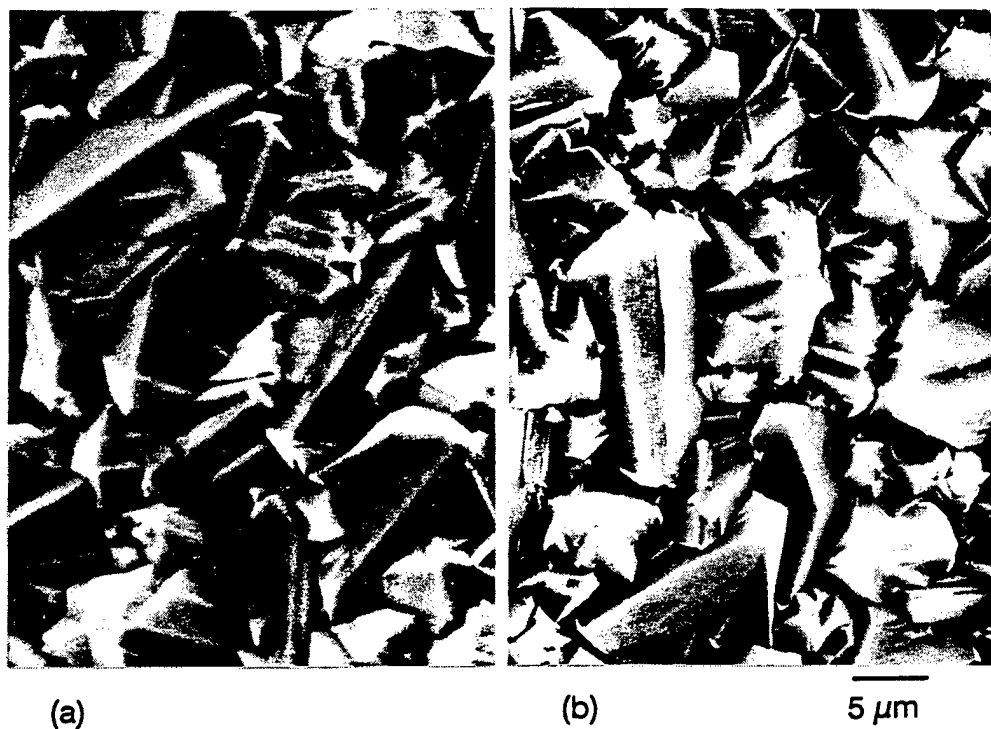


Fig.5. (a) and (b) are SEM images of the diamond films deposited at CH_4 concentrations of 5% and 7%, respectively, at the filament temperature of 2600°C and the filament-substrate distance of 1 mm. The reactor pressure was 200 Torr. The substrate holder temperature was 700°C. (c) The growth rates of the diamond films shown in (a) and (b).

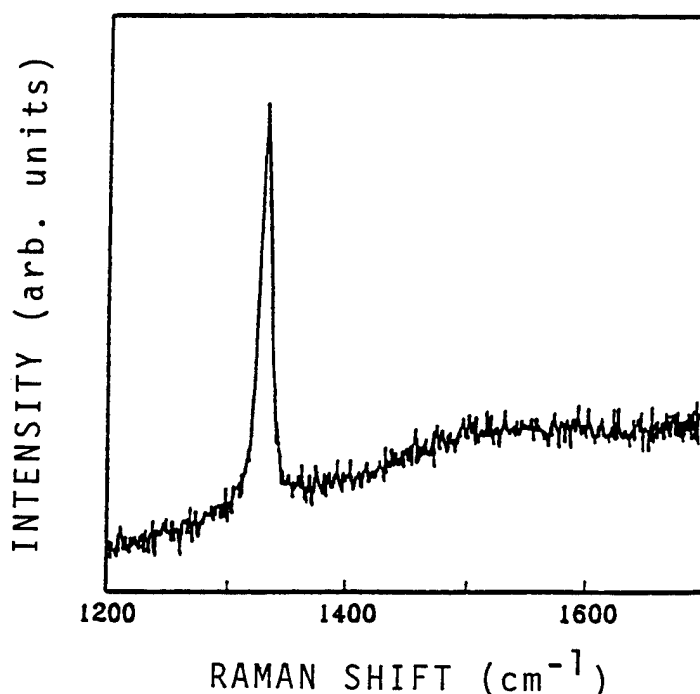


Fig. 6. Raman spectrum of the diamond film shown in Fig.5(b).

growth rates can thus be achieved using a higher CH_4 concentration. The growth rate was also increased by decreasing the filament-substrate distance. High filament temperature and short filament-substrate distance are advantageous for high-rate deposition of high-quality diamond films. High-quality diamond films with a growth rate higher than $16 \mu\text{m/h}$ have been obtained at the filament temperature of 2600°C , filament-substrate distance of 1 mm, CH_4 concentration of 7%, and at a reactor pressure of 200 Torr using the hot-filament CVD technique.

Acknowledgments

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Growth of diamond by sequential deposition and etching process using hot filament CVD

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High quality diamond films with enhanced growth rates have been grown by a sequential deposition and etching process using the hot filament CVD method. A computer is used to control the switching between a cycle of high methane-content gas mixture diluted with hydrogen, which is used for high growth rate deposition, and the other cycle of hydrogen gas only, which is used for non-diamond etching, in order to achieve high growth rate diamond deposition without sacrificing diamond quality. According to SEM and Raman spectroscopy, high quality diamond films are obtained by use of a suitable ratio of the deposition time to the etching time and a short cycling period (10 s), which is necessary to remove undesirable non-diamond components in time to grow high quality diamond. The growth rate is several times higher than that of diamond film with a similar quality deposited by the continuous diamond deposition condition using the hot filament CVD method.

1. Introduction

Diamond films have been grown heterogeneously on non-diamond substrates by various chemical vapor deposition (CVD) techniques [1–6] from the beginning of 1980's. Hot filament CVD is one of the oldest and the major method for depositing high quality CVD diamond on large area. The typical reaction gas is methane–hydrogen mixture. High quality diamond films can be grown at low methane concentrations (lower than 1%) in hydrogen [2], but the growth rate is low. Atomic hydrogen, an important species in CVD diamond formation, is known to play one of its roles of effectively etch non-diamond components that are co-deposited with diamond during the deposition [7]. The crystallinity of diamond strongly depends upon the etching effect of atomic hydrogen, especially when a high carbon concentration gas mixture is applied.

A sequential deposition and etching process [8,9] has been applied to the oxy-acetylene combustion flame CVD [10] and microwave plasma CVD [9] to deposit high quality diamond using a high carbon-content gas mixture. In this study, we used a computer to control the reaction gas mix-

ture between the high methane concentration diluted in hydrogen for the deposition part and the hydrogen only for the etching part of the alternate cycles in order to deposit high quality diamond at a higher growth rate using a hot filament CVD system. To achieve a high growth rate deposition, a higher methane concentration in hydrogen than that usually used to deposit high quality diamond by the continuous deposition process was introduced into the reaction chamber during the deposition cycle. During the etching part of the cycle, only the hydrogen gas was introduced to promote the etching of the non-diamond components that were deposited simultaneously with diamond during the deposition cycle.

2. Experimental procedure

The experiments were carried out in a hot filament CVD system as shown in fig. 1. A computer controls a 3-way solenoid valve that is used to either introduce methane to the reaction chamber, thus creating a high growth rate deposition, or to vent the methane to the vacuum pump,

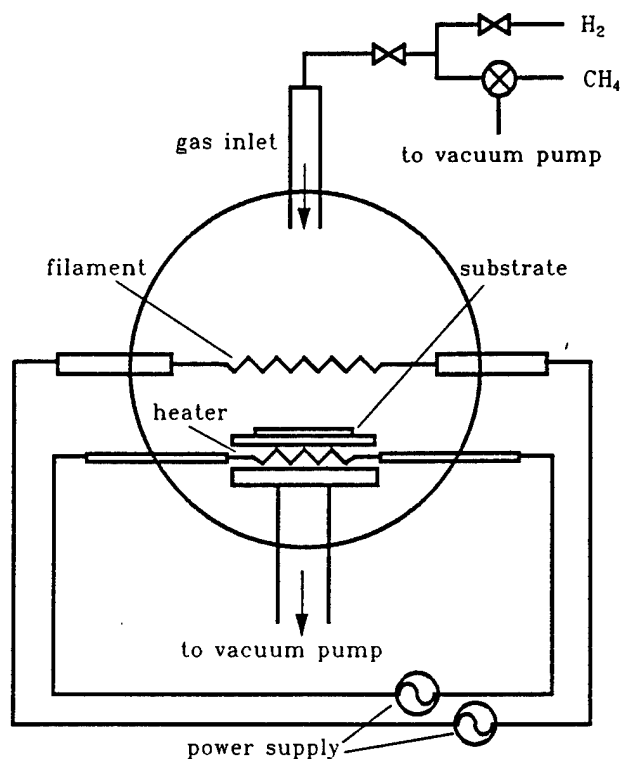


Fig. 1. Schematic diagram of hot filament CVD system.

thus allowing only hydrogen to be fed into the reaction chamber and creating a net etching reaction. The cycling frequency was controlled by the computer.

Silicon substrates were polished with 1 μm diamond paste before deposition. The reaction chamber was evacuated to 20 mTorr before the reaction gases (CH_4 diluted with H_2) were introduced into the reaction chamber. The reactor pressure was set at 50 Torr. The total gas flow rate ranged from 200 to 500 SCCM. The hot filament is made of a tungsten wire of 1 mm in diameter and the temperature was about 2100–2400°C. The substrate temperatures were 600 to 1000°C, and controlled both by the hot filament and a tantalum heater. The substrate temperatures were measured by a thermocouple inserted into the graphite substrate holder. The deposited films were characterized by scanning electron microscope (SEM) and Raman scattering spectroscopy.

3. Results and discussion

In the sequential deposition and etching process, the ratio of deposition cycle time to etching cycle time (T_D/T_E) is one of the important parameters. Fig. 2 shows the Raman spectra for diamond films deposited under different cycling conditions. The different deposition times used were 5, 10, 20, and 30 s while the etching time was kept constant at 10 s. The reaction gases were CH_4 (3%) + H_2 (97%) for the deposition cycle, and was 100% H_2 for the etching cycle. The substrate temperature was 750°C. Diamond Raman peaks at 1332 cm^{-1} are shown in figs. 2a–2d. A broad background around 1550 cm^{-1} attributed to non-diamond carbon is found in figs. 2a and 2b for specimens formed with longer deposition times (T_D/T_E are 3 and 2, respectively). This is because the etching time is not sufficient to completely remove non-diamond phases deposited during the longer deposition cycle time. The formed diamond films thus contain non-diamond components. In such cases, the growth rates are high. However, figs. 2c and 2d show that by keeping the etching time constant and decreasing the deposition time to 10 and 5 s, high quality diamond films are obtained (T_D/T_E are 1 and 0.5, respectively), with slightly lower growth rates, especially for the case of 5 seconds deposition cycle time. It is considered that, the amount of the non-diamond components formed during the deposition cycle decreases with decreasing deposition cycle time, and therefore can be more completely etched away in the subsequent etching cycle. By decreasing the T_D/T_E ratio, the growth rate decreases slightly, but greatly enhances the quality of the diamond film. Using the present system set up, the suitable ratio of T_D/T_E was found to be 1:1 for depositing high quality diamond films with higher growth rates.

The formation of diamond films by the sequential deposition and etching process also depends strongly on the cycling frequency. Fig. 3 shows the SEM photographs of diamond films deposited with different cycling times at 750°C and $T_D/T_E = 1$. The same gas feed condition for deposition and etching cycles as mentioned ear-

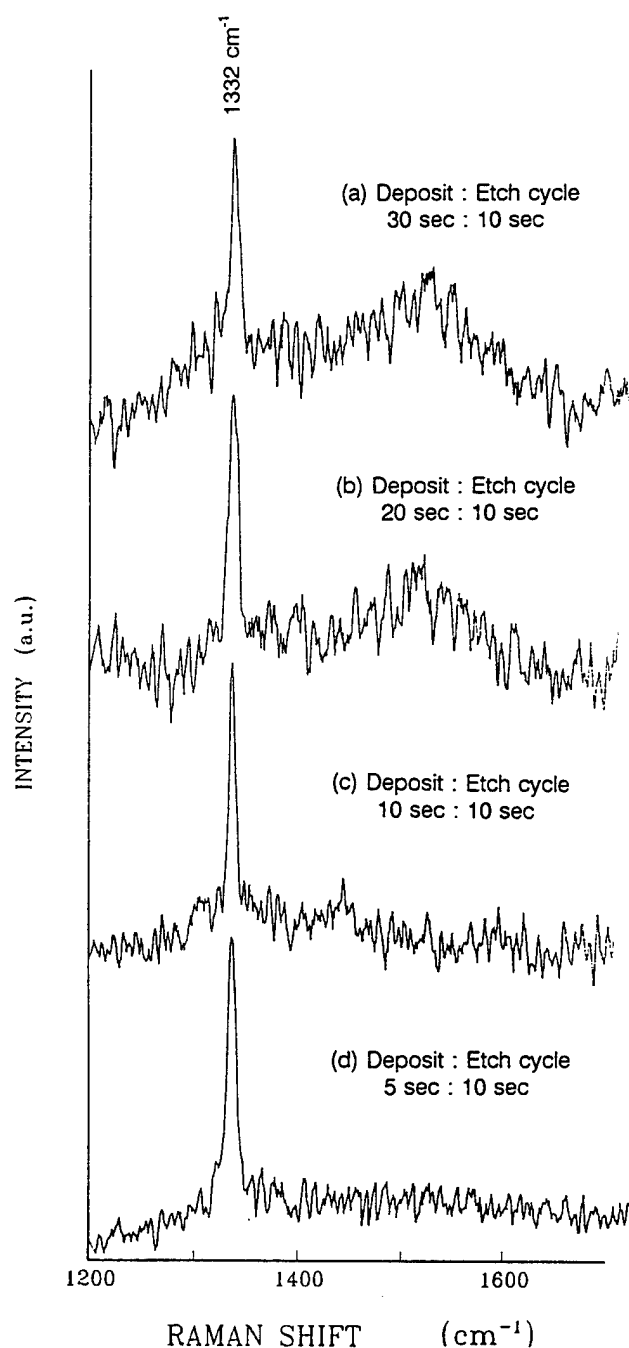


Fig. 2. Raman spectra of films deposited by the sequential deposition and etching process at 750°C. The etching time was fixed at 10 s, while the deposition times of (a), (b), (c), and (d) were 30, 20, 10, and 5 s, respectively.

lier was used. At a longer cycling time of 2 min deposition and 2 min etching (fig. 3a), a lot of small particles (secondary nucleations) were found on the surface. By decreasing the cycling time to

10 s deposition and 10 s etching, diamond films with clear and well faceted diamond particles were obtained as shown in fig. 3d. A shorter cycling time suppresses secondary nucleation and small particle growth, and is advantageous to diamond film deposition with larger grain sizes and clearer crystal facets.

The crystallites of diamond films shown in fig. 3 were examined by Raman spectroscopy as shown in fig. 4. Fig. 4a is a Raman spectrum of the film shown in fig. 3a. It shows an intense diamond peak at 1332 cm^{-1} and a broad non-diamond carbon peak around 1550 cm^{-1} . By decreasing the cycling time, the ratio of the signal intensity around 1550 cm^{-1} to that at 1332 cm^{-1} is decreased. For a shorter cycling time condition consisting of 10 s deposition and 10 s etching, high quality diamond film was obtained. The Raman spectrum is shown in fig. 4d and has only a sharp diamond peak at 1332 cm^{-1} . It is believed that with a higher methane concentration and longer cycling time, a lot of non-diamond components (graphite and amorphous carbon) are simultaneously deposited with diamond during the longer deposition cycle and not all of the non-diamond components can be completely etched away during the relatively short etching cycle. Thus, non-diamond components are left over and subsequently buried in the growing diamond film. Therefore, the diamond film contains non-diamond components. Whereas with a shorter cycling time, non-diamond components formed during the shorter deposition cycle can be more completely etched away during the etching cycle leaving only high quality diamond for further growth in the next deposition cycle. High quality diamond films can be grown by continuing this cyclic process. By controlling the cycling time, high quality diamond films with well faceted diamond particles have thus been obtained with high methane concentration.

Due to the removal of non-diamond components in the growing films, the growth rate of the diamond film decreases with decreasing cycling time. According to SEM and Raman spectra obtained, the growth rate of the diamond film deposited with 10 s deposition and 10 s etching is still 2.5 times higher than that for diamond films



Fig. 3. SEM micrographs of diamond films deposited on Si substrates at 750°C with different cycling times. Deposition time: etching time was (a) 2 min:2 min, (b) 1 min:1 min, (c) 30 s:30 s, and (d) 10 s:10 s.

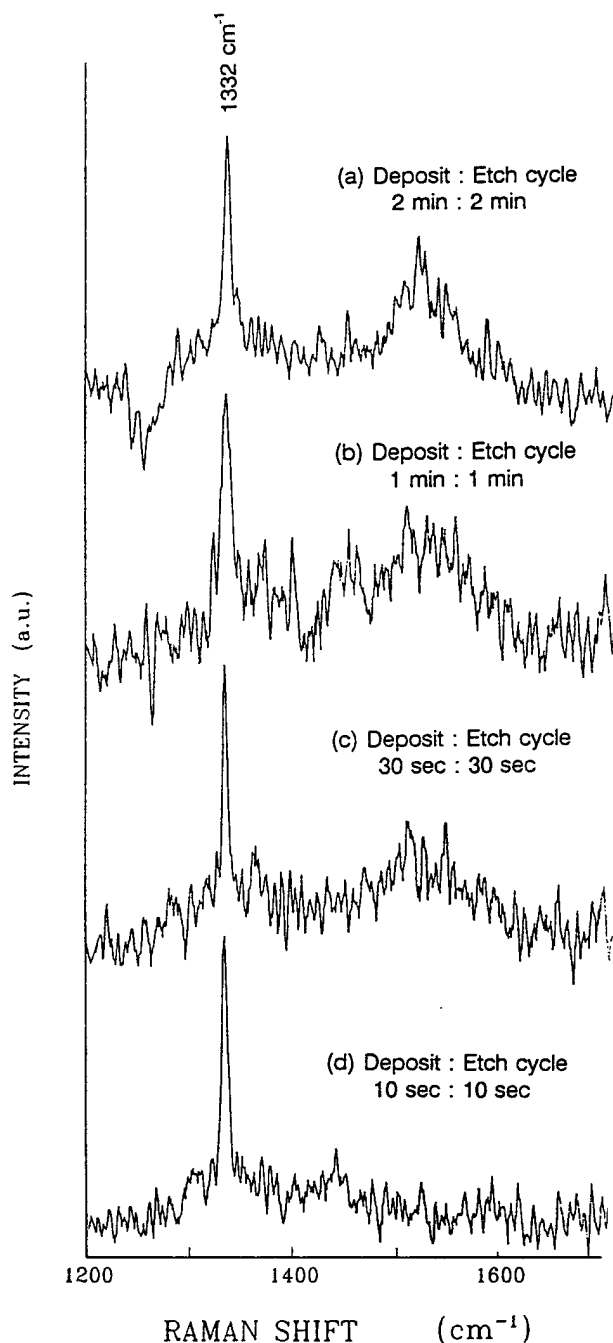


Fig. 4. Raman spectra for diamond films shown in Figs. 3a, 3b, 3c and 3d, respectively.

with similar quality deposited by the continuous diamond deposition process, which requires a low methane concentration of 0.7% CH_4 in H_2 . With the sequential deposition and etching process, higher methane concentrations can be used for high quality diamond deposition with higher

growth rates than that deposited by the continuous deposition process using the hot filament CVD method.

4. Conclusions

A sequential deposition and etching process is used to deposit high quality diamond films with high growth rates, using the hot filament CVD system. During the deposition cycle, a high methane concentration diluted in hydrogen was used for high growth rate diamond deposition, and during the etching cycle, pure hydrogen was used to etch the non-diamond components. It was found that the crystallites of the diamond films strongly depended on deposition and etching cycling times. For short cycling times i.e., 10 s deposition and 10 s etching, high quality diamond films were deposited with growth rates several times higher than what was achievable using the continuous deposition process that produced similar diamond quality in the same system. This sequential deposition and etching process is advantageous to grow diamond films using a high carbon concentration without sacrificing the quality of the diamond film.

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High quality flame-deposited diamond films for IR optical windows

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Abstract

The IR absorption in polycrystalline diamond films deposited in oxygen–acetylene flames was characterized using the Fourier transform IR spectroscopy (FTIR). The one-phonon absorption coefficient in the region from 7 to 12 μm that is related to extrinsic defects in the diamond films shows a strong dependence on the flame conditions as well as the substrate temperature. A high degree of diamond crystalline perfection, as judged from the undetectable one-phonon absorption, is achieved under the optimized deposition conditions for our flame set-up. This is further supported by the sharp Raman peak at 1332 cm^{-1} as well as the high purity in crystal orientation according to the X-ray diffraction pattern measured for the high quality diamond films. Optimal deposition conditions produce diamond films with a lower degree of secondary nucleation than is found in the lower quality diamond deposits.

1. Introduction

Long-wave IR (LWIR) optical systems require high transmittance in the 8–12 μm band. High purity type IIa diamond is not only free of the intrinsic absorption in this wavelength band [1] but also has superior thermal conductivity and chemical inertness as well as mechanical strength that make it unsurpassed by other optical materials such as ZnS, ZnSe, and germanium in optical applications involving severe thermal shock and erosion.

Although diamond has no intrinsic absorption in the 8–12 μm range, impurities and defects in the diamond can induce significant amounts of absorption that renders these less perfect diamonds useless as windows for LWIR optical systems. As a matter of fact, the majority (98%) of all clear diamonds found in nature have large absorption coefficients in the 7–12 μm range [1] owing mainly to nitrogen impurity induced absorption, which is also used as one way of distinguishing type I from type II diamond [2].

The absorption band related to two-phonon absorption processes is the only band detected in high quality type II natural diamond. The absorption coefficient of diamond in this two-phonon band is relatively insensitive to impurities and has a value of 12.3 cm^{-1} at 5 μm [1], which will be used as a reference for the normalization of the measured IR absorption spectra in this paper.

Although high quality diamond optical windows can be made of selected natural diamond crystals, the small size of natural diamond and the high cost of such

a component restrict the use of it to special cases in which no other choices are available. The limitation in the size of diamond optical windows has possibly been eliminated thanks to the recent success of growing diamond films on foreign substrates from carbon-containing gases by means of various kinds of chemical vapor deposition (CVD) techniques. These CVD processes are capable of depositing polycrystalline diamond films at subatmospheric pressures and at substrate temperatures lower than 1000 $^{\circ}\text{C}$ under thermodynamically non-equilibrium conditions.

CVD diamond films show IR spectra that are affected by scattering owing to surface roughness and internal defects. Diamond films deposited by the microwave plasma CVD method have been reported to have one-phonon absorption coefficients at 7.5 μm (1332 cm^{-1} , the Raman line of diamond) ranging from 4.2 cm^{-1} to 33 cm^{-1} [3]. These films might still be useful for thin protective coatings of LWIR optical windows but are far from being acceptable for thick (2.5 mm for example) antireflection (AR) coated diamond windows that require transmittance as high as 93%. The detected one-phonon absorption band in CVD diamond increases with increasing absorption coefficients in the “C–H stretch” region with peaks at 2848 cm^{-1} and 2915 cm^{-1} , which are believed to be caused by antisymmetric and symmetric C–H₂ stretching vibrations respectively [4, 5]. The hydrogen responsible for this C–H stretch absorption in CVD diamond is associated with some kind of structural defects in the diamond lattice and cannot be annealed out at temperatures as high as 1500 $^{\circ}\text{C}$ [3].

Atomic hydrogen appears to be needed for all known methods of diamond CVD processes. Although hydrogen contamination seems to coexist with both the C-H stretch absorption as well as the one-phonon absorption, it is the structural defects in the diamond lattice that must be minimized in order to eliminate or at least reduce these IR absorption bands in CVD diamond. The reported low absorption due to the C-H stretch and small one-phonon absorption for CVD diamond epitaxial layers grown on type IIa natural diamond support this [6]. The spectra of these CVD homoepitaxial films have one- and two-phonon absorption and C-H stretch bond vibration similar to type IIa natural diamond. Homoepitaxial diamond films have the good optical quality needed for thick LWIR optical windows. However, the major restriction, *i.e.* the small size of natural diamond substrates, in the use of natural diamond as LWIR optical windows remains. It is therefore necessary to develop an optimal diamond CVD process that can deposit thick, high quality diamond films onto inexpensive foreign substrates of any desired shape and area.

2. Experimental details

Among a number of diamond CVD methods, the flame CVD [7] using an oxygen-acetylene mixture has been reported to deposit diamond films with high electrical resistivity ($10^{14} \Omega \text{ cm}$) [8] and good optical transparency in the LWIR wavelength region [9]. Although a single-tip oxyacetylene torch can only deposit diamond films smaller than 1 cm in diameter, scaling-up of such a process has been reported to be feasible [10, 11]. In this paper we will report the optimization of the flame CVD process for depositing diamond films of high quality, as well as discuss the correlation between the IR absorption spectra, Raman spectra, X-ray diffraction pattern, and scanning electron microscope images measured for the flame-deposited diamond films. The experimental set-up has been reported previously [8].

3. Results and discussion

The parameter space that is studied to achieve the high quality diamond film includes the carbon-to-oxygen ($[\text{C}]/[\text{O}]$) ratio for the flame and the substrate temperature. Among many possible combinations of these two process parameters, nine experimental conditions near the optimal point for diamond growth are shown in Fig. 1. The comparison of the IR absorption spectra for a good sample (sample 4) and a poor sample (sample 3) is shown in Fig. 2. Sample 4 is

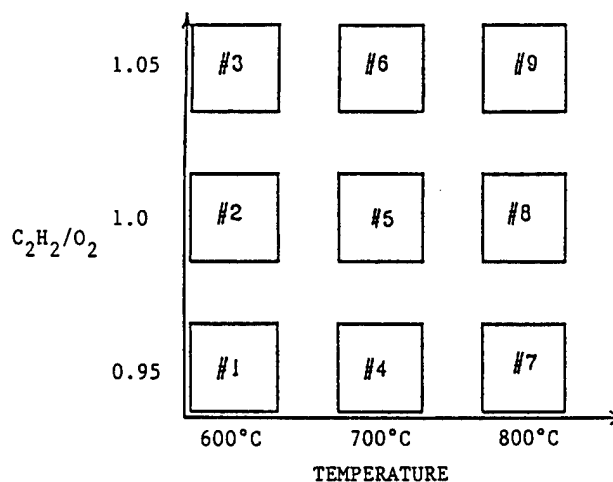


Fig. 1. Parameter space investigated as a function of substrate temperature and acetylene to oxygen mass flow ratio ($[\text{C}_2\text{H}_2]/[\text{O}_2]$). The conditions under which each sample was deposited are shown.

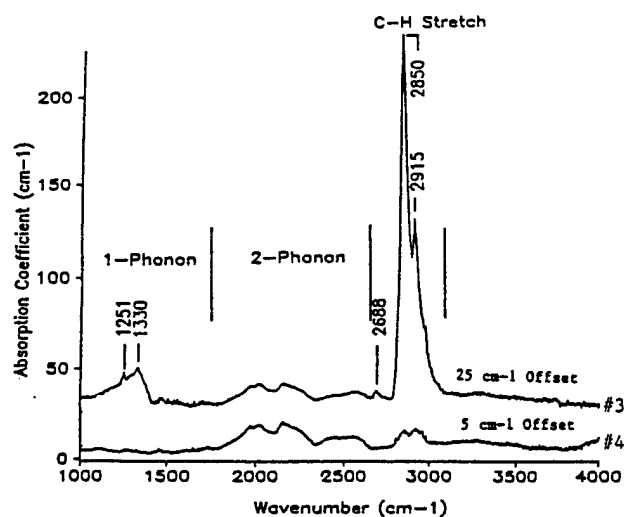


Fig. 2. IR absorption spectra for sample 3 (top) and sample 4 (bottom).

deposited using a $[\text{C}]/[\text{O}]$ ratio less than unity and a medium substrate temperature while sample 3 is deposited at a higher $[\text{C}]/[\text{O}]$ ratio and a lower substrate temperature. It can clearly be seen from Fig. 2 that sample 3 has a high concentration of defects along with a high hydrogen contamination level as is indicated by the strong C-H stretch band and the large one-phonon absorption coefficients. In the C-H stretch band, the 2850 cm^{-1} peak is significantly more intense than the 2915 cm^{-1} peak. This is opposite to what is observed for diamond films deposited in $\text{CH}_4\text{-H}_2$ mixtures without adding oxygen. When a small amount of oxygen is added to the $\text{CH}_2\text{-H}_2$ mixture, the 2850 cm^{-1} peak

becomes stronger than the 2915 cm^{-1} peak. This latter case is consistent with the C-H stretch band for flame-deposited diamond films that are grown in an oxygen environment. Oxygen apparently affects the incorporation of hydrogen into the CVD diamond film. It favorably reduces the density of defects that will trap atomic hydrogen to cause one-phonon absorption as well as C-H stretch absorption. The IR optical transparency appears to improve with the addition of oxygen. As a matter of fact, the one-phonon absorption band for sample 4 cannot be detected using the Fourier transform (FT) IR system available for this work. The C-H stretch band for sample 4 is even smaller than the intrinsic two-phonon band that also exists in high quality type IIa natural diamond. Sample 4 indicates that the flame-deposited diamond films have the IR optical quality that might be sufficient for thick LWIR window applications. Final proof of this prediction requires depositing thick (greater than 1 mm) diamond films with an IR transparency comparable with that shown for sample 4.

Figures 3, 4, and 5 shows the absorption coefficients of the symmetric C-H stretch (2915 cm^{-1}), the anti-symmetric C-H stretch (2848 cm^{-1}), and the one-phonon absorption band for the diamond films deposited under different conditions as shown in Fig. 1. The trend of an increasing one-phonon absorption with increase in hydrogen contamination induced C-H stretch absorption is clearly seen in these figures. It appears that a relatively low [C]/[O] ratio less than unity is needed to deposit diamond films of high LWIR optical quality by the flame method. A substrate temperature that is not too low is also necessary.

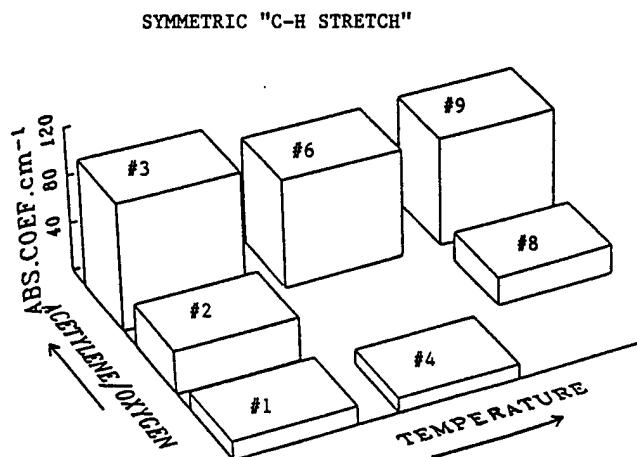


Fig. 3. Comparison of the absorption coefficients of the symmetric C-H stretch (2915 cm^{-1}) taken from the IR absorption spectra of the samples described in Fig. 1.

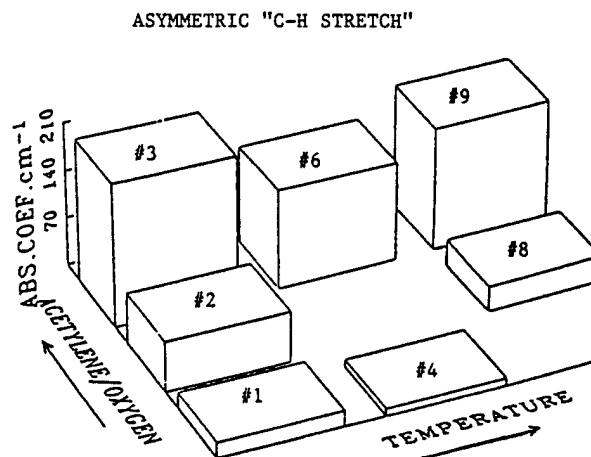


Fig. 4. Comparison of the absorption coefficients of the asymmetric C-H stretch (2848 cm^{-1}) taken from the IR absorption spectra of the samples described in Fig. 1.

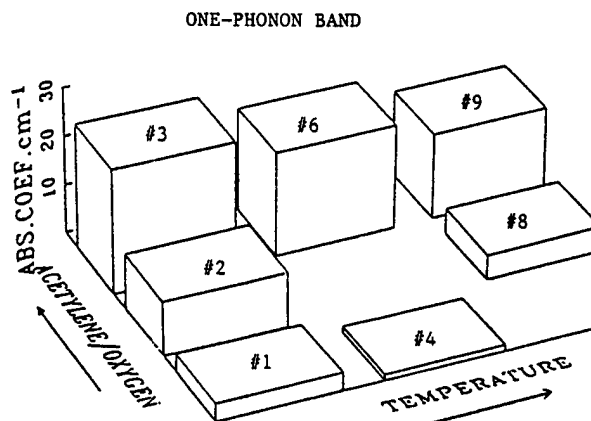


Fig. 5. Comparison of the absorption coefficients of the one-phonon band taken from the IR absorption spectra of the samples described in Fig. 1.

The comparison of the Raman signal among the same set of samples is shown in Fig. 6, which displays the ratio of the Raman signal intensity at 1332 cm^{-1} to that at 1520 cm^{-1} . The correlation between the large Raman peak ratio and the small one-phonon and C-H stretch absorption coefficients can clearly be seen by comparing Fig. 6 with Figs. 3–5. The sample showing the strongest Raman peak at 1332 cm^{-1} with a low background signal at 1520 cm^{-1} is the best sample for LWIR optical window applications.

The X-ray diffraction patterns taken for sample 4 and sample 3 are shown in Fig. 7. It shows that the good sample 4 has a strong (111) peak while the rest of the peaks for (110), (100), (220), (311), (400), and (311) orientations are very small. In contrast, the X-ray diffraction pattern for the poor sample 3 has comparable intensities for peaks corresponding to (111), (220),

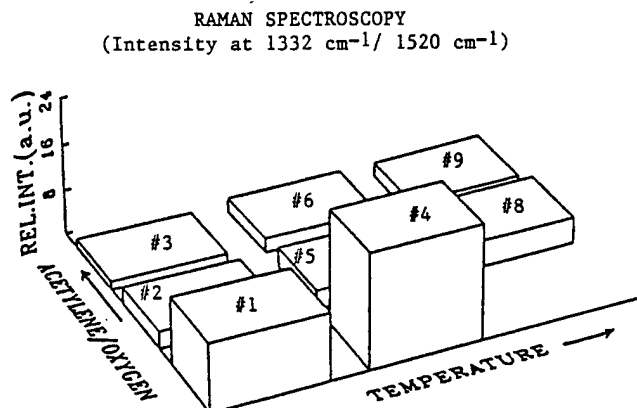
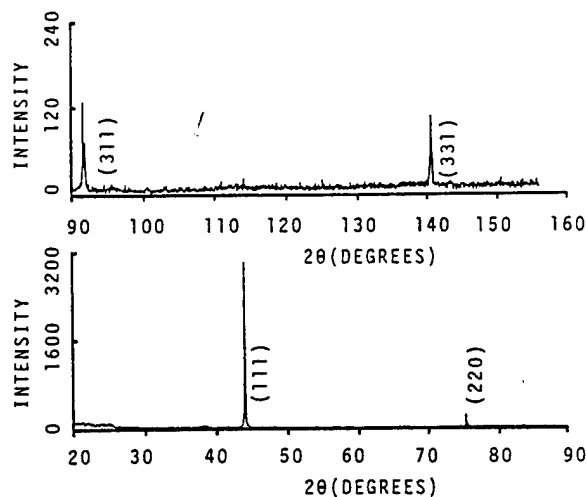
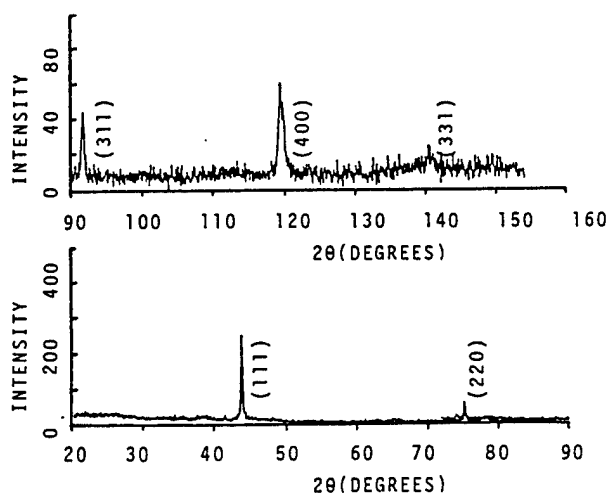


Fig. 6. Comparison of the ratio of the Raman signal intensities at 1332 cm⁻¹ (diamond signature peak) to that at 1520 cm⁻¹ (peak for non-diamond phases) for the samples described in Fig. 1.



(a)



(a)

Fig. 7. X-ray diffraction taken from (a) sample 4 showing the purer crystal orientation (*i.e.* dominant (111) orientation), and (b) sample 3 showing the comparable intensities for several crystal orientations.



Fig. 8. SEM images of (a) sample 4 showing the well faceted (111) crystals with low secondary nucleation, and (b) sample 3 showing the secondary nucleation present on the diamond crystals.

(311), and (400) orientations. This indicates that sample 4, which has the best LWIR quality, also has the purest crystal orientation in the film.

Comparing the corresponding scanning electron microscopy (SEM) images of samples 3 and 4 (see Fig. 8), one can see that the secondary nucleation rate is low for a [C]/[O] ratio less than unity, as was used to deposit sample 4. The higher [C]/[O] ratio combined with the lower substrate temperature used in depositing sample 3 led to a higher secondary nucleation rate and more pronounced multiple crystal orientations, as evidenced by the X-ray diffraction pattern. In order to achieve a diamond film of high LWIR optical quality, secondary nucleation or defect-enhanced diamond growth processes should be avoided or at least controlled.

4. Conclusions

Diamond films with low "C-H stretch" absorption coefficients and undetectable one-phonon absorption

can be achieved by proper optimization of the oxy-acetylene flame deposition conditions. The optimal conditions used to deposit LWIR quality diamond films also yield low secondary nucleation rates and low deposition rates. In addition, the optimal deposition conditions yield samples with the strongest Raman peak at 1332 cm^{-1} with respect to the background broad band at 1520 cm^{-1} , and a pure crystal orientation, *i.e.* (111), as measured by the X-ray diffraction method. The low secondary nucleation rate accounts for the pure crystallinity in the film. Although high quality diamond films can be deposited onto foreign substrates at the expense of a low growth rate corresponding to the low $[\text{C}]/[\text{O}]$ ratio, further research and development is needed to increase the growth rate and growth area without sacrificing the quality of the diamond films.

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